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VOLATILIZATION LOSSES OF PESTICIDES FROM SOILS

Walter J. Farmer, et al

California University

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VOLATILIZATION LOSSES OF PESTICIDES FROM SOILS

Farmer, Walter J., and Letey, John

University of California
Riverside, California

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Temperature gradients in soil significantly affected the distribution of volatile pesticides in soil. Vapor phase diffusion toward areas of low temperature can occur simultaneously with mass flow in liquid water toward areas of high temperature.

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VOLATILIZATION LOSSES OF PESTICIDES FROM SOILS

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ABSTRACT

The volatilization of pesticides following soil application can be predicted from considerations of the physical and chemical principles controlling concentrations at the soil surface. When these concentrations are maintained at a relatively high level, volatilization losses will be determined by the pesticide vapor pressure as modified by adsorptive interactions with the soil. For pesticides which have been mixed with the soil or when volatilization has been proceeding for a time so that concentrations at the soil surface are low, volatilization rates will be determined by the rate at which pesticides move through the soil to the soil surface. Under conditions when mass flow in liquid water is negligible, volatilization rates are predictable using solutions to the diffusion equations. When mass flow is operative the prediction of rates of volatilization are more complex. A computer model has been developed combining both diffusion and mass flow for predicting the volatilization of soil-incorporated pesticides.

Temperature gradients in soil significantly affect the distribution of volatile pesticides in soil. Vapor phase diffusion toward areas of low temperature can occur simultaneously with mass flow in liquid water toward areas of high temperature.

This report was submitted in fulfillment of Grant No. R-801835, Program Element 1BB039 by the Department of Soil Science and Agricultural Engineering, University of California, Riverside, under the sponsorship of the Environmental Protection Agency. Work was completed as of April 1974.

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The development of the diffusion based models for predicting the volatilization of soil-incorporated pesticides was performed and written by Dr. Robert Mayer while he was a post-doctoral fellow at the University of California Riverside.

Dr. Fritz Huggenberger initiated the investigation into the effect of temperature gradients on pesticide movement in soils while he was a post-doctoral fellow at the University of California Riverside. Dr. Robert Mayer completed and wrote up the investigations reported here.

Dr. Vern Weeks was primarily responsible for development of the computer program for the combined diffusion and mass flow model for predicting volatilization of soil-incorporated pesticides.

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SECTION I

CONCLUSIONS

1. Pesticide volatilization from soils can be modeled. The choice of model to use will depend on pesticide characteristics, application techniques, and climatic factors such as surface wind speed.

2. For soil-incorporated pesticides which have significant mobility in flowing water, a computer based model is utilized to predict pesticide volatilization. A numerical solution of the mass flow and diffusion equations is required for the model.

3. The volatilization of soil-incorporated pesticides which have limited mobility in flowing water can be predicted using an analytical solution to the diffusion equations. Five different models have been developed depending on the initial and boundary conditions which can be applied to the situation. The solutions to these diffusion-based models are relatively simple when compared to the mass flow model.

4. When pesticides remain on the soil surface as in the case of non-incorporated pesticides, vapor density relationships and air flow rate rather than movement in the soil becomes the factor controlling the rates of volatilization. Rates of volatilization of surface applied pesticides can be predicted on the basis of pesticide vapor pressure following calibration with a known pesticide.

5. The effect of temperature gradients on pesticide movement in soils can be investigated experimentally. Water flow characteristics in soils due to temperature gradients must be determined to understand pesticide movement. Significant pesticide flow toward areas of low temperature due to vapor diffusion and toward areas of high temperature due to mass flow with water can occur simultaneously.

SECTION II

RECOMMENDATIONS

1. Pesticide losses due to volatilization of soil applied pesticides can be drastically reduced by rapid incorporation into the soil following application. Most of the loss due to volatilization takes place within the first few hours following application. Volatilization is directly related to soil concentration. Rapid reduction of the concentration of the pesticide at the soil surface by incorporation will greatly reduce volatilization. An application of only one kg/ha can result in very high soil concentrations at the soil surface if not incorporated.

2. Calibration of existing pesticide volatilization models with field trials should greatly improve their accuracy. Data from field volatilization trials will also indicate how improvements can be accomplished in the models.

3. A great deal of study is needed on the effects of temperature gradients, rainfall events, photodecomposition, and degradation rates on the concentration of pesticide at the soil surface. The concentration at the soil surface is probably the greatest factor affecting rates of volatilization and many factors influence this concentration. For example, the frequency, intensity, duration and amounts of precipitation determine how much pesticide remains on the soil surface for volatilization to take place and how much is removed by run-off or leaching and therefore less subject to subsequent volatilization.

SECTION III

INTRODUCTION

The quantities of pesticides entering our rivers, lakes, and streams are of vital concern to those dedicated to preserving environmental quality. Those pesticides which eventually find their way into our rivers and lakes are rapidly dispersed over wide geographic areas due to the rapid intermixing of water. This rapid dispersal allows intimate contact of pesticides with a number of organisms including man, wildlife, crops and other flora and fauna especially those adapted to life in an aquatic environment. The present state of our knowledge indicates the major mechanism by which pesticides enter waterways from treated land surfaces is by run-off. A second source of less magnitude is by rain-out of air-born pesticides. Whatever the source of pesticides in water, it will be necessary to adequately describe the fate of pesticides applied to land surfaces before reliable predictions can be made of amounts of pesticides entering waterways and to establish adequate management practices to control these losses.

Pesticide volatilization is one mechanism by which pesticides may be lost from soils. Other mechanisms include drift, run-off, decomposition (biological, non-biological, photochemical), leaching into groundwater, and plant uptake. From a quantitative point-of-view, the predominant mechanism operating at any particular time will depend on a number of factors including soil characteristics, vegetative cover, environmental conditions and type of pesticide. Most situations in which pesticides appear require a knowledge of how each mechanism is operating to account for the dissipation of all pesticides applied.

The purpose of this project is to define and describe those factors which are most significant in controlling pesticide volatilization from soil surfaces and to formulate these factors into a mathematical model for predicting pesticide volatilization from treated soil. A volatilization model is to be developed that can be used to simulate vapor loss under a variety of soil, watershed, and environmental conditions. It is intended that the models herein developed will be useful in an overall transport model for predicting quantities of soil-applied pesticides which are lost due to run-off.

SECTION IV

FACTORS CONTROLLING PESTICIDE VOLATILIZATION FROM THE SOIL SURFACE

Before describing the factors influencing volatilization it is necessary to discuss how pesticides get into the atmosphere and to define volatilization. Pesticides may be present in the atmosphere due to drift, volatilization, or pesticide-laden soil particles carried there by wind action. Drift results during spray applications when wind blown spray particles are carried away from the target area. The major portion of a pesticide which gets into the atmosphere takes place at the time of application. This is due both to drift particles that never reach the ground and to pesticides reentering the atmosphere by volatilizing after reaching the target area. Thus, by volatilization, the inference is that the pesticide is in the atmosphere in the true vapor phase. Pesticides will also be in the vapor phase by volatilization from the spray droplets before reaching the target. Once pesticides volatilize either from spray particles or from the target surface they may recondense as pesticide particles, spray particles, on air-borne dust, or on adjacent land and plant surfaces. Both pesticide drift and wind blown dusts contribute significant amounts of pesticides in the atmosphere under certain conditions. However, this project will deal only with volatilization from land surfaces as this is the primary pathway of entry into the atmosphere following application.

Volatilization as used here will mean the loss of pesticides from treated soils by evaporation into the true vapor phase followed by movement into the atmosphere above the soil. Volatilization from plant surfaces may follow many of the same principles. Since most of the available information is on volatilization from soils, this project will deal only with soil-applied pesticides.

The literature relating to pesticide volatilization was recently reviewed by Spencer, Farmer and Cliath (1973). The reader is referred to this review for a discussion of the evidence pointing toward pesticide volatilization as a significant factor. In addition the article presents a detailed discussion of the mechanisms and factors that influence volatilization rates. Grover et al. (1973) have discussed the significance of pesticide drift and its relationship to volatilization. Finklestein (1969) has presented an extensive review on concentrations of pesticides in air.

In order for a pesticide to volatilize from soil, three things must take place: 1) pesticide molecules within the soil must move to the soil surface, 2) the pesticide molecule must be present in the vapor phase at the soil surface and 3) the pesticide molecule must move away from the soil surface into the atmosphere above the soil. If the rate at which any of these processes takes place decreases, the rate of volatilization will also decrease. The rate of volatilization will then be controlled by the factors influencing these three processes.

Movement of pesticide molecules to the soil surface may be either in the vapor or non-vapor phases. The mechanism of movement to the soil surface may be either by diffusion or by mass flow. The literature on the movement of pesticides in soil has been recently reviewed by Letey and Farmer (1974). Movement to the soil surface will become a limiting factor when pesticide molecules at the soil surface are depleted and the only way in which additional pesticide can volatilize is by movement from deeper in the profile.

Once pesticides reach the soil surface their potential for volatilization will depend on their vapor phase concentration or vapor density. [Vapor density is related to the vapor pressure by the equation for perfect gases, $p = d\,(RT/M)$, where p is vapor pressure, d is vapor density, R is the molar gas constant, T is the absolute temperature, and M is the molecular weight of the pesticide. In this report vapor density will be used interchangeably with the term saturation vapor concentration (S.V.C.) as used by Hartley (1969)]. Each pesticide compound has a characteristic vapor pressure. When a pesticide is applied to a surface its vapor pressure, and therefore its vapor density, will be reduced depending on the extent of adsorption which takes place between the pesticide and the surface. The literature on the factors controlling the vapor density of adsorbed pesticides has been extensively reviewed by Spencer, Farmer and Cliath (1973). Briefly, the two most significant factors affecting vapor density, in addition to the temperature effect, are soil pesticide concentration and soil water content. Non-polar and weakly polar pesticides are strongly adsorbed by dry soils. Thus a pesticide may diffuse to the soil surface in the vapor phase and be adsorbed so that the rate of volatilization is zero. However, for soil water potentials greater than approximately -15 bars, pesticide volatilization is independent of soil water content and is dependent on pesticide concentration in the soil water. Pesticide vapor density will increase with increasing concentration until the maximum vapor pressure of the pesticide is reached.

The last hurdle for a pesticide to cross before it can volatilize is to move away from the soil surface so additional molecules can move into the vapor phase. The rate of movement away from an evaporating surface will be dependent to some extent on the rate of diffusion in air. However, this step in the volatilization process will normally be limiting only in cases of high pesticide concentration on the soil surface or when there is no wind activity and the air above the soil is stable and quiet.

Any factors, such as surface wind speed, which tends to remove pesticides from the site of evaporation should cause an increase in the rate of volatilization. Several investigators have found the rate of volatilization of pesticides to be directly related to air flow over the evaporating surface (Harris and Lichtenstein, 1961; Danielson and Genter, 1964, Parochetti and Warren, 1966; Harthy, 1969; Farmer et al. 1972). On the other hand, factors which may retard pesticide

dissipation in the atmosphere would be expected to reduce volatilization. Most of the studies of pesticide volatilization rates have been performed with bare soils. The presence of a cover crop, and the type of cover and its density, would reduce wind speed and turbulence at the soil surface and therefcre should reduce volatilization. Pesticide movement by diffusion in air would be expected to be slower than movement by air currents.

Sufficient information appears to now be available on factors affecting pesticide volatilization to attempt formulating predictive models. Knowledge of the particular conditions existing in the field hopefully will allow the selection of the proper model to use.

SECTION V

THEORETICAL CONSIDERATIONS

Based on the steps involved in the volatilization processes as discussed in the previous section, the modeling of pesticide volatilization from soils can be divided into three separate cases. In the first instance, the volatilization of surface applied pesticides is considered. In this case, the rate of volatilization will be dependent on the vapor pressure of the pesticide itself, temperature and wind speed. In the second and third instances soil-incorporated pesticides are considered and the rate at which pesticides move to the soil surface is the rate-limiting step in volatilization. In the second case, only diffusion is considered and in the third situation, mass flow and diffusion are considered together in moving pesticides to the soil surface.

SURFACE APPLIED PESTICIDES

Pesticide volatilization will normally be highest during and immediately following application. This will be especially true when the application is not incorporated into the soil by disking or other appropriate means. When the pesticide is exposed on the surface of the soil it will be subject to rapid volatilization. The following considerations were designed to model those factors which determine the rate of volatilization of surface-applied pesticides.

It is assumed that the volatilization of a pesticide from a soil surface is related to the molecular diffusion coefficient of the compound in air. According to Fick's first law, the rate of molecular diffusion will be proportional to the diffusion coefficient and to the saturation vapor concentration (S.V.C.).

$$q = K_l D_v \Delta c_a / L \qquad [1]$$

where q = rate of diffusion, K_l is the constant for the geometry of the soil, D_v = vapor diffusion coefficient, Δc_a is the vapor concentration gradient, and L is the length over which diffusion occurs. When the pesticide is on the soil surface K_l is equal to one. For the case when $K_l \neq 0$, see section pertaining to soil-incorporated pesticides.

Assuming air flow and turbulence maintain zero concentration at distance, d, above the pesticide treated area,

$$\Delta c_a = c_a = \text{S.V.C.} \qquad [2]$$

Hartley (1969) has indicated an inverse proportionality of the diffusion coefficient to the square root of the molecular weight (M).

$$D_v = K_2/M^{\frac{1}{2}} \qquad [3]$$

where K_2 is a proportionality factor.

Combining equations [1], [2], and [3]

$$q = -K_v \text{ S.V.C. } M^{-\frac{1}{2}} \qquad [4]$$

where $K_v = K_1K_2/d$.

From the perfect gas laws the vapor concentration is proportional to the vapor pressure (p) times the molecular weight.

$$c_a = pM/RT \qquad [5]$$

where R is the gas constant and T is the absolute temperature.

Combining equations [1], [2], [3] and [5]

$$q = K_v' \, pM^{\frac{1}{2}} \qquad [6]$$

where $K_v' = -K_1K_2/RTd$. The rate of diffusion or the rate of volatilization, f, will be proportional to the vapor pressure times the square root of the molecular weight. Alternatively, according to Equation [4], the volatilization rate will be proportional to the saturation vapor pressure divided by the square root of the molecular weight of the pesticide.

DIFFUSION BASED MODEL FOR SOIL-INCORPORATED PESTICIDES

When the pesticide concentration at the soil surface is reduced or depleted, pesticide must move to the surface if volatilization is to take place. In the absence of appreciable mass transfer due to water movement, diffusion processes in the soil will account for the movement of pesticides to the soil surface to replace that lost by volatilization. The objective of this portion of the project is to develop mathematical equations for predicting volatilization of soil-incorporated pesticides as a diffusion controlled process and compare calculated with measured results. This portion of the study is published separately (Mayer, Letey, and Farmer, 1974).

The basic assumption in the mathematical treatment of the movement of pesticides in soils under a concentration gradient is the applicability of the diffusion laws. The changes in pesticide

concentration within the soil as well as the loss of pesticides at the soil surface by volatilization can then be predicted by solving the diffusion equation for different boundary conditions. Recognizing the analogy between the heat transfer equation (Fourier's law) and the transfer of matter under a concentration gradient (Fick's law), solutions of the heat transfer equation given by the mathematical theory of conduction of heat may be used. The mathematical model for predicting volatilization of pesticides is then given as a set of boundary conditions sufficient to solve the diffusion equation.

Consider a system where a pesticide is uniformly mixed with a layer of soil and volatilizing at the soil surface. If diffusion is the only mechanism supplying pesticide to the surface, and if we assume isotropic conditions in the soil as well as constancy of the diffusion coefficient D, then the general diffusion equation is

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D}\frac{\partial c}{\partial t} = 0 \qquad [7]$$

where c is the pesticide concentration in the soil (g cm^{-3} total volume), x the distance measured normal to the soil surface (cm), D the diffusion coefficient (cm^2 sec^{-1}) and t the time (sec).

Model I

As a first approximation we may assume that pesticide volatilizes and is removed rapidly maintaining a zero concentration at the soil surface. The depth of the soil layer treated uniformly with pesticide is L, and the initial concentration C_o (g/cm^3). The initial and boundary conditions for which equation [7] is to be solved are then:

$$c = C_o \text{ at } t = 0,\ 0 \leq x \leq L$$

$$c = 0 \text{ at } x = 0 \text{ and } t > 0$$

$$\partial c/\partial x = 0 \text{ at } x = L$$

Carslaw and Jaeger [1959, p. 97, equation (8)] give a solution for these boundary conditions that can be used by accepting the following analogies:

v (temperature) = c (concentration)

V_o (initial temperature) = C_o (initial concentration)

κ (thermal diffusivity)
K (thermal conductivity) } = D (apparent diffusion coefficient)

The concentration units for c and C_o must be expressed on a total volume basis in order for D to be analogous to K and κ.

The solution for equation [7] is then

$$c = \frac{4C_o}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \{\exp[-D(2n+1)^2\pi^2 t/4L^2]\} \cos \frac{(2n+1)\pi(L-x)}{2L} \qquad [8]$$

(Carslaw and Jaeger used the boundary condition x = L and we have used x = 0 at the soil surface. Identical results are achieved by our using (L - x) in the equations where Carslaw and Jaeger used x). The pesticide flux, f ($g/cm^2/sec$), through the surface is given as the concentration gradient at x = 0 times the diffusion coefficient, D:

$$f = D[\partial c/\partial x]_{x=0} = \frac{DC_o}{(\pi Dt)^{\frac{1}{2}}} \left[1 + 2\sum_{n=1}^{\infty} (-1)^n \exp(-n^2L^2/Dt)\right] \qquad [9]$$

Model II

The summation term in equation [9] decreases with increasing L and decreasing D and t. If this term is small enough to be negligible, equation [9] reduces to

$$f = DC_o/(\pi Dt)^{\frac{1}{2}} \qquad [10]$$

This equation is identical with the solution given by Carslaw and Jaeger [1959, p. 59, equation (3)] for heat flow in an infinite solid. The concentration for the semi-infinite case is given by

$$c = C_o \mathrm{erf}[x/2(Dt)^{\frac{1}{2}}] \qquad [11]$$

Equations [10] and [11] are applicable also on a finite system (in the region $0 < x < L$) as long as the concentration at the lower boundary of the soil layer, x = L, is not decreased by pesticide moving in the upward or downward direction. To estimate the maximum time at a given set of parameters for which Model II is adequate, let us assume the critical value to be a drop of 1% in the initial concentration, C_o, at the lower boundary of the soil layer. With this assumption the boundary conditions used in deriving equation [11] are violated if

$$\mathrm{erf}[L/2(Dt)^{\frac{1}{2}}] \leq .99$$

or

$$t > L^2/14.4\ D$$

Model III

Model I assumed that no diffusion occurs across the lower boundary x = L. This boundary condition is appropriate for laboratory studies which will be reported later, but not realistic for field conditions where diffusion can occur downward across the boundary x = L. The boundary conditions for the latter case are

$$c = C_o \text{ at } t = 0,\ 0 \leq x \leq L$$

$$c = 0 \text{ at } t = 0,\ x > L$$

$$c = 0 \text{ at } t > 0,\ x = 0$$

Solution of equation [7] with these initial and boundary conditions is given by Carslaw and Jaeger [1959, p. 62, equation (14)] as

$$c = (C_o/2)\left\{2\ \mathrm{erf}[x/2(Dt)^{\frac{1}{2}}] - \mathrm{erf}[(x-L)/2(Dt)^{\frac{1}{2}}] - \mathrm{erf}[(x+L)/2(Dt)^{\frac{1}{2}}]\right\} \quad [12]$$

The flux is obtained by differentiating equation [12] with respect to x, determining $\partial c/\partial x$ at x = 0, and multiplying by D. The result is

$$f = [DC_o/(-Dt)^{\frac{1}{2}}][1-\exp(-L^2/4Dt)] \quad [13]$$

Note that equation [13] reduces to equation [10] for large values of $L^2/4Dt$. Less than 1 per cent error will result from using equation [4] if

$$\exp(-L^2/4Dt) < .01$$

or

$$t < L^2/18.4\ D$$

Model IV

The solutions for the diffusion equation become more difficult if the concentration at the soil surface is variable instead of being maintained at zero. The rate of removal of pesticide in the air layer above the soil may then become a limiting factor in the rate of volatilization.

A model which accounts for a possible imcomplete depletion at the soil surface may be described as follows. A soil layer ($0 \leq x < L$) has a uniform initial distribution of pesticide C_o with no flux allowed through the lower boundary at $x = L$. The soil surface, $x = 0$, is in contact with a volume, V, of well stirred air (uniform concentration within the air) from which a volume per unit time and unit area, v, is withdrawn and replaced by the same volume of air at zero concentration. The airflow thus removes an amount of pesticide which is equal to the flow velocity, v, times the concentration within the air, c_a. The initial and boundary conditions are

$$c = C_o \text{ at } t = 0,\ 0 \leq x \leq L$$

$$\partial c/\partial x = 0 \text{ at } x = L$$

$$f = v\, C_a \text{ at } t > 0,\ x = 0$$

This model is analogous to that of Carslaw and Jaeger [1959, p. 129, equation (11)] in which a slab of uniform initial temperature is in contact with a mass per unit area of well-stirred fluid which loses heat by radiation at a rate H times its temperature. The initial temperature of the fluid is zero C. Their solution is

$$c = 2C_o \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)(h-k\alpha_n^2)\cos[\alpha_n(L-x)]}{[L(h-k\alpha_n^2)^2 + \alpha_n^2(L+k)+h]\cos\alpha_n L} \qquad [14]$$

where α_n are the roots of

$$\alpha \tan(\alpha L) = h - k\alpha^2 \qquad [15]$$

Carslaw and Jaeger define $h = H/K$ where K is the thermal conductivity. For our case K is replaced by the diffusion coefficient, D, and H by the air flow velocity, v.

The concentration in the air, c_a, must be expressed in terms of the concentration at the soil surface, c_s. This is done by the use of the absorption isotherm. Adsorption isotherms for lindane and dieldrin given in literature (Spencer and Cliath, 1970; Spencer, Cliath and Farmer, 1969) suggests that we may, for a small concentration range

of c_s consider the isotherm as

$$c_a = R\, c_s \qquad [16]$$

Thus, h in equation [14] appears to be

$$h = Rv/D \qquad [17]$$

(Note that both concentrations c_a and c_s in [16] must be expressed on a total volume basis).

The term k, appearing in equation [14] is defined by Carslaw and Jaeger as the ratio of the heat content of the fluid to the heat content of the slab. The ratio in the heat flow model is equal to R in equation [17] so that

$$k = R \qquad [18]$$

It can be shown that for all cases treated here

$$k \ll h \text{ or } k\alpha_n^2 \ll h.$$

Equations [14] and [15] can therefore be simplified to

$$c = 2C_o \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)h \cos[\alpha_n(L - x)]}{(Lh^2 + \alpha_n^2 L + h)\cos \alpha_n L} \qquad [19]$$

and

$$\alpha \tan(\alpha L) = h \qquad [20]$$

The pesticide flux through the soil surface at x = 0 is then given by

$$f = 2DC_o \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)\, h^2}{Lh^2 + \alpha_n^2 L + h} \qquad [21]$$

Carslaw and Jaeger (1959, p. 491) give a table of the first six roots

of the equation

$$\alpha \tan \alpha = M \qquad [22]$$

which can be used instead of [20] when L = 1 or by scaling all variables containing units of length in terms of L.

Model V

Model IV assumes the air above the soil to be sufficiently stirred that its concentration may be taken to be constant throughout. This may be due to turbulence as well as to a large diffusion coefficient within the air. However, Model IV does not take into account any diffusive transfer of pesticide. When air velocity becomes zero, the predicted flux through the soil surface becomes zero as well. This model thus can only be appropriate if the convective flow due to air movement is considerably greater than the flow due to a diffusion gradient.

If there is a non-moving air layer in contact with the soil surface, the following model may be adequate. The diffusion coefficient of a pesticide in air is D' and the thickness of the air layer is d. As a first approximation we may neglect the capacity of the air layer. For example, Spencer and Cliath (1970) report that at 30 C a soil with 10^4 ng/cm^3 lindane is in equilibrium with a lindane vapor density in air of .22 ng/cm^3. Then, if the concentration in soil at the soil surface is c and the concentration in air at the soil surface is Rc, we have the flux through the air layer given by

$$f = D' Rc/d$$

when the concentration at the upper edge of the air layer is zero. The initial and boundary conditions are

$$c = C_o \text{ at } t = 0,\ 0 \leq x \leq L$$

$$\partial c/\partial x = 0 \text{ at } x = L$$

$$f = (D'Rcs)/d \text{ at } t > 0,\ x = 0$$

$$c = c_s \text{ at } t > 0,\ x = 0.$$

These conditions are equivalent to the "radiation" boundary conditions described by Carslaw and Jaeger (1959). We may than adopt the solution given by these authors [p. 316, equation (24)] after substituting h in their equations by

$$h = D'R/Dd \qquad [23]$$

The concentration of pesticide in soil is

$$c = \frac{2D'RC_o}{Dd} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)\cos[\alpha_n(L-x)]}{[L(D'R/Dd)^2 + L\alpha_n^2 + D'R/Dd]\cos\alpha_n L} \qquad [24]$$

$$\text{with } \alpha \tan(\alpha L) = D'R/Dd \qquad [25]$$

The flux through the soil surface at x = 0 is

$$f = 2DC_o \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)(D'R/Dd)^2}{L(D'R/Dd)^2 + L\alpha_n^2 + D'R/Dd} \qquad [26]$$

Note that equations [24], [25], and [26] are identical with equations [19], [20], and [21], but instead of

$$h = Rv/D$$

we have defined h by equation [23].

MODEL BASED ON DIFFUSION AND MASS FLOW OF SOIL-INCORPORATED PESTICIDES

As stated for the diffusion based model, movement to the soil surface becomes the limiting factor in determining pesticide volatilization when the concentration at the soil surface is depleted. The objective of this portion of the project is to include both diffusion and mass flow in a mathematical model for predicting volatilization of soil-incorporated pesticides.

For vertical, isothermal flow in a homogeneous porous material, the flow equation is

$$\frac{\partial\theta(h)}{\partial h}\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left(K(h)\frac{\partial h}{\partial z}\right) + \frac{\partial K(h)}{\partial z} \qquad [27]$$

h is the pressure head of water in the porous material, measured in cm of water, z is the depth below the surface and is positive in the upward direction measured in cm, t is the time in days, $\partial\theta(h)/\partial h$ is the specific water capacity, where $\theta(h)$ is the volumetric water content of the porous media measured as a function of the pressure head measured in cm^3 of water/cm^3 of total space, K(h) is the water conductivity as a

function of pressure head expressed in cm/day. The boundary and initial conditions analyzed were as follows:

$$h = h_o \exp(-0.29^t) \text{ at } z = 0 \text{ and } \underline{t \geq 0} \qquad [28]$$

until $h = -1.456 \times 10^6$ cm = relative humidity = 0.35 at 23 C, then h remained constant

$$-K(h)\ (\partial h/\partial z + 1) = 0 \text{ at } z = -L \text{ and } \underline{t > 0} \qquad [29]$$

$$h = -300(\text{cm of water}) - z \text{ or } (\partial h/\partial z + 1) = 0 \text{ for}$$

$$-L \leq z \leq 0 \text{ at } t = 0 \qquad [30]$$

Equation [28], where h_o is the initial value of h at z = 0, represents an empirical condition that when used to solve Equation [27] gave calculated water outflow data that closely approximated corresponding experimental values obtained when K(h), $\partial\theta(h)/\partial h$, and $\theta(h)$ were determined for Gila silt loam. L in Equation [30] represents the length of a soil column in this case.

For vertical, isothermal movement of pesticide in a homogeneous porous material the flow equation is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\ D_{vs}(\theta)\ \frac{\partial c}{\partial z} - \frac{\partial}{\partial z}\ (V(\theta)\ C') \qquad [31]$$

where C is total mass/cm^3 of total space, (C = mass in soln + mass adsorbed per cm^3), t is the time in days, z is depth below the surface, $D_{vs}(\theta)$ is the total apparent diffusion coefficient as a function of $\theta(h)$, in cm^2/day, $V(\theta)$ is the water velocity in the pores of the media as a function of $\theta(h)$ in cm/day, C' is the mass in soln/cm^3 of porous material. The boundary and initial conditions were

$$C = C_o \exp(-20t) \text{ at } z = 0 \text{ and } t \geq 0 \qquad [32]$$

$$C = 0,2 \text{ cm below z where } C \neq 0 \text{ and } t \geq 0 \qquad [33]$$

$$C = C_o = \rho_b(10\ \mu g/g \text{ soil}) \text{ at } 10 \leq z \leq 0 \text{ and } t = 0 \qquad [34]$$

ρ_b = average bulk density of soil (gm soil/cm^3 total space)

Equations [27] and [31] were solved by numerical analysis. The method of finite differencing the terms in equations [27], [29] and [31] and the method of solving the resulting equations, has been given

in a number of papers by Whisler and Klute (1965), Klute, Whisler and Scott (1965), and Whisler and Klute (1967).* The method involves an interative procedure in which estimates of h (z) were calculated from previous estimates at each value. The initial conditions of the problem provided the first estimates for the first time step. Final estimates for each time step were the first estimates for the next time step, etc. The final estimates for a particular time step were determined by comparing each particular estimate with the previous estimate; if the absolute values of all the differences were less than some small selected value or if a given number of iterations was exceeded, the final estimates were accepted and the solution proceeded to the next part of the problem.

Data relating K, $\frac{\partial\theta(h)}{\partial h}$, and θ to h were obtained experimentally in the laboratory by the method described by Weeks and Richards (1967). Values of h(z,t) were calculated for each time step. From these values, corresponding values of θ (z,t) were obtained by linear interpolation of the θ(h) data, and values of the hydraulic head [H(z,t)], were H(z,t) = h(z,t) + z, were calculated. Hydraulic gradient values, ∇H(z,t), were calculated by numerical differentiation, and the macroscopic water velocity (v(z,t)) was calculated from: v(z,t) = -K(h,z) ∇H(z,t). Then the water velocity in the pores, V(θ), was calculated from: V(θ) = v(z,t)/θ(z,t).

Equation 31, with the initial and boundary conditions [Equations 32, 33 and 34] was solved for C(z,t) by the same method as in the case of equation 27. Experimental values of $D_{vs}(\theta)$ were taken from the report of Shearer, et al. (1973). Their data were obtained at 30 C and the individual $D_{vs}(\theta)$ values were divided by 2 for use in the present study since the relations between K, C, θ, and h were obtained in this case in a room where temperature and relative humidity were not controlled but remained close to 23 C and 35% respectively during the time of the work. Earlier work of Ehlers et al. (1969) indicates that D_{vs} values for 23 C are approximately one-half those for 30 C for lindane and Gila silt loam. In solving equation [31], C', the liquid phase concentration was expressed in one of two ways at each position (z) depending on whether adsorption or desorption occurred at a particular position since the previous time. Values of the adsorbed phase concentration $[C(z) - C'(z)]_{m-1}$ were compared with $[C(z) - C'(z)]_m$ values, where m refers to the present time step. When desorption was indicated,

$$C(z)_i = C(z)_i \Big/ \left[1 + \rho_b \left(\frac{K}{\theta(z)}\right)^N \left(\frac{S\ max(z)}{C'(z)_{i-1}}\right)^{1-N}\right] \qquad [35]$$

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*Appreciation is expressed to F. D. Whisler, formerly Soil Scientist-Physicist, U.S. Water Conservation Laboratory, Phoenix, Ariz., now Professor of Soil Physics, Mississippi State University, Oxford, Miss., for the use of his unpublished programs which were modified when necessary and were used in this study.

where K is the constant relating adsorbed and solution phases with units of cm^3 liquid/g soil, $S_{max}(z)$ is the maximum value of the adsorbed phase concentration (mass of material/gm soil) obtained at a given z. N is the ratio between the values of exponents of C' (N desorption/N adsorption) in the Freundlich equation. The use of K^n and S_{max} in this way was taken from Van Genuchten et al. (1974). N was taken to be 0.4 also from Van Genuchten et al. (1974) as near the midrange of their values for N adsorption/N desorption (2.3 to 3.1 for picloram). N adsorption was taken to be 1 and K = 2.875 cm^3 liquid/g soil from Huggenberger et al. (1972). In the case of adsorption,

$$C'(z)_i = C(z)_i/[1 + \rho_b K/\theta(z)] \qquad [36]$$

The subscript, i, in equations [35] and [36] refers to a value of the variable calculated at the present iteration; i - 1, refers to a value from the previous iteration.

The final estimates of C(z) were used to calculate C'(z) values for each time step using equations [35] or [36], and corresponding adsorbed phase concentration values, S(z), were calculated by difference. That is,

$$S(z) = C(z) - C'(z). \qquad [37]$$

Cumulative outflow of water or pesticide was calculated by integrating numerically:

$$\text{Outflow} = \int_{-L}^{0} f(z,o)dz - \int_{-L}^{0} f(z,t)dz \qquad [38]$$

where f(z,o) represents initial values and f(z,t) represents values of the particular material at time t.

The rate of outflow of pesticide (at chosen times) was determined by numerical differentiation of the values represented by the integrals in equation [38] for the chosen times.

EFFECT OF TEMPERATURE GRADIENT ON PESTICIDE MOVEMENT

Numerous studies have been performed separately on the diffusion and mass flow of pesticides in soils. (Ehlers, et al., 1969; Farmer and Jensen, 1969; Oddson, Letey and Weeks, 1970; Huggenberger, Letey and Farmer, 1972). However, in actual field situations these two processes will occur simultaneously; and only by studying these two processes together will we arrive at a solution which will allow us to predict the actual movement in the environment. The objective of this research was to create an experimental system, where both transport processes occur simultaneously in order to demonstrate the relative importance of diffusion and mass flow as transport processes for pesticides under different experimental conditions. By applying a temperature gradient on a soil column, which has a uniform initial moisture and pesticide content, such a situation is achieved. The vapor pressure of any substance increases with increasing temperature. A vapor pressure gradient is therefore established from the warm to the cold end of the soil column. Consequently, water and pesticide molecules will move from the warm to the cold end of the column in the vapor phase. This transfer of water vapor will then create a suction gradient and cause liquid water and dissolve pesticide molecules to move in the opposite direction by mass flow. In a closed system, as studied here, the transfer of water vapor from the warm to the cold end and the transfer of liquid water from the cold to the warm end are equally at steady state. Transfer of pesticide molecules as discussed above will also create a concentration gradient of the pesticides in the nonvapor phase. Consequently, transfer of pesticide molecules will also occur by nonvapor diffusion (Ehlers, et al., 1969).

At this point it is not possible to quantitatively predict the experimental results by theoretical consideration. By considering pertinent soil and pesticide properties an effort is made however, to explain the experimental results quantatively.

SECTION VI

EXPERIMENTAL DESIGN

The rates of volatilization of dieldrin from treated soil and of dieldrin, lindane, trifluralin, DDT and DDE from treated quartz sand were measured in a closed air-flow system by collecting volatilized pesticide in vapor traps. Chemical designations of pesticides cited in the text are given in Table 1. Concentrations of dieldrin on Gila silt loam were 5, 10, 20 and 30 $\mu g\ g^{-1}$ soil (oven dry weight equivalent). Concentration of pesticide on sand was 1000 $\mu g\ g^{-1}$ sand. Separate samples of sand were used for each pesticide. A modification of the method for measuring volatilization of pesticide given by Farmer, et al. (1972) was used. A brief outline along with modifications is given here. The metal soil tray described by Farmer et al. (1972) was replaced with a plexiglass tray having a soil surface area of 18.49 cm^2 and a soil depth of one cm. The soil and sand matrix were treated with pesticides in hexane, the hexane allowed to evaporate and water added to the matrix to the desired water content. The treated soil or sand was placed in the plexiglass tray and the tray introduced into the vapor trapping apparatus. When it was desired to maintain a constant soil water content during the volatilization experiment, the relative humidity of the air was kept near 100% by passing the incoming air through fritted glass bubblers in water traps. Relative humidities were checked with a hygrometer built into the air stream. Air flow rates were controlled with needle valves installed in a manifold and measured by a soap bubble flow-meter at the end of the trapping system. The entire vapor trapping apparatus was located inside a constant temperature incubator and temperature controlled to ±0.5 C. The soil was Gila silt loam containing 0.58% organic matter and 17.6% clay, predominantly montmorillonite. The quartz sand was acid-washed with dilute HCl and washed with distilled water to pH 7. The pesticide was extracted from the trapping medium, either ethylene glycol or hexylene glycol, by watering into hexane. An aliquot was then analyzed by liquid scintillation analysis or gas-liquid chromatography. For gas-liquid chromatography a one meter by 3 mm stainless steel column was used with 2.5% DC-200 plus 2.5% QF-1 on Chrom W80-100 mesh support, column temperature of 200 C for dieldrin, DDE, and DDT and 183 C for lindane, and a flow rate of 50 ml N_2 per minute.

EFFECT OF TEMPERATURE GRADIENT ON PESTICIDE MOVEMENT

The pesticides used in this study were lindane, diuron, and atrazine. ^{14}C-labeled diuron and atrazine were used in this study.

The purity of lindane was checked by gas liquid chromatography. The development of degradation products was insignificant over the period of time the compound was used. The purity of ^{14}C-labeled and unlabeled diuron and atrazine was checked by thin layer chromatography using silica gel GF 254 containing a fluorescent indicator. The solvent systems for diuron were distilled water and a 1:1 (v/v) mixture

Table 1. CHEMICAL DESIGNATIONS OF PESTICIDES CITED IN TEXT.

atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine
DDE	1,1-dichloro-2,2,2-bis(p-chlorophenyl) ethylene
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane
dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4, 4a,5,6,7,8,8a-oxtohydro-1,4-endo-exo-5,8-dimethanonaphthalene
diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
lindane	γ-1,2,3,4,5,6-hexachlorocyclohexane
trifluralin	α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine

of distilled water and acetone. The solvent systems for atrazine were a mixture of petroleum ether, ethylacetate, and acetic acid 30:50:1 (v/v) and a mixture of hexane and acetone 150:45 (v/v). The plates were examined under UV light. Only one spot could be detected in all replications. In the trials using ^{14}C-labeled materials the activity of this spot was determined by liquid scintillation and accounted for more than 95% of the total activity applied. It was concluded that all the materials were pure and therefore used without further purification.

The soil materials used were the <1-mm fraction of Gila silt loam and Pachappa sandy loam. Gila silt loam has an organic matter content of 0.65% and a clay content of 18.4%. Pachappa sandy loam has an organic matter content of 0.87% and a clay content of 12.6%.

Lindane in hexane, diuron in acetone and atrazine in chloroform were added to the respective soils to the desired concentrations with an atomizer. The soil was then aerated for 24 hours to remove the solvents. The water content was adjusted to the desired levels by adding a predetermined amount of 0.01 N KCl solution. The soil was then packed into a piece of acrylic tubing of cross sectional area (A) of 46.3 cm^2, length (L) 21 cm and wall thickness of 0.35 cm. The bulk density (β), the gravimetric water content (P_w) (g of water/g of oven-dry soil, and the pesticide concentration in microgram of pesticide per gram of oven-dry soil (C_o) in the soil columns were determined at the beginning of the experiments. The ^{14}C-activity in columns 2 and 3 was 2500 dpm/g oven-dry soil. Preliminary experiments have shown that at the start of the experiments these values were uniform throughout the soil columns.

The soil columns were installed in a horizontal position and tensiometer cups (Coors Porcelain Co., No. P-3-C, porosity 1.5-2.2 microns columns 2 and 3) were installed in holes drilled for them at distances of 2.0, 5.5, 11.0 and 19.0 cm from the warm end of the columns. The initial suction heads (h_o) along the columns were measured. Thermocouples (copper constantan) were installed in small holes at distances of 1.0, 5.5, 11.0, 15.5 and 20.3 cm from the warm end of the columns. The columns were sealed to prevent the loss of water at all boundaries and thermally insulated around the cylindrical wall with coarse vermiculite. A heat source was applied at one end of the columns. After the desired temperature gradients (∇T) were established, this gradient was maintained for 36 days for column 1 and for 20 days for columns 2 and 3. At the termination of these periods, the soil columns were sectioned. The water contents, pesticide contents and the Cl^- concentration of the saturation extracts of individual sections were then determined.

Soil samples containing lindane were extracted with a hexane: acetone (41:59) azeotrope on a Soxhlet extractor. The extracts were then analyzed by gas liquid chromatography. The gas chromatograph used was a Varian Aerograph Model 1520B with solid state electrometer. The

91.4 cm (3 ft.) stainless steel column was packed with 2.5% DC 200 and 2.5% QF-1 on chromosorb W 80/100 mesh size. Detection was by electron capture. The column temperature was 192 C, the flow rate 50 ml/min and the resulting retention time for lindane 1.5 min. The ^{14}C-activity of soil samples containing diuron and atrazine was determined by liquid scintillation. An aliquot of soil of individual sections was placed directly into counting vials. Twenty milliliters of a scintillation solution consisting of 10.4 g of PPO and 166 g naphthalene dissolved in a solution of 800 ml of xylene, 800 ml of dioxane, and 473 ml of absolute ethanol were added. To avoid a special procedure of extraction the ^{14}C-activity was determined in the presence of soil. This method has been reported and discussed in detail by Ehlers et al. (1969). Pesticide and Cl^- concentrations are reported as microgram per gram of oven-dry soil.

SECTION VII

RESULTS AND DISCUSSION

SURFACE APPLIED PESTICIDES

The volatilization of surface applied pesticides was simulated using pesticide treated sand. At the high rate of pesticide used, 1000 μg per gram of sand, the sand was acting only as a carrier and exerted essentially no adsorptive forces on the pesticide.

The volatilization of trifluralin, lindane, p,p'-DDE and p,p'-DDT from treated sand are shown in Table 2. Reasonable agreement was obtained between the volatilization rate and the saturation vapor concentrations of the pesticides as determined by the relationship shown in equation [4]. In this case, the pesticide flux, f, is used in place of the rate of diffusion, q.

$$f = K_v(S.V.C.)M^{-\frac{1}{2}} \qquad [39]$$

The value of K_v ranged from 119 to 133.

The rate of pesticide volatilization is also dependent on the rate of air movement across the treated surface. In a separate study the air flow rate was varied between 120 and 960 ml min^{-1}. In this experiment the air space above the treated sand in the volatilization chamber was 214 ml. In the previous study (Table 2) the air space above the treated surface was 24.4 ml. Increasing the air space reduces the air flow velocity across the treated surface at any given air flow rate. The results of this experiment are shown in Table 3. As in the previous study there is good agreement between K_v and S.V.C. at any given flow rate. However, K_v and therefore the pesticide flux increased linearly with increasing flow rate. The slope of the line was 0.11 with an intercept K = 31.5 and a correlation coefficient of 0.96.

An additional comparison can be made from the data in Tables 2 and 3. There was an average increase of 70% in the K_v values in Table 3 when the air flow rate was doubled from 480 to 960 ml min^{-1}. In order to obtain a similar increase in K_v in Table 2, the air flow velocity was increased 7.5 times (2.82 cm sec^{-1} vrs. 0.374 cm sec^{-1} at 480 ml min^{-1} air flow rate).

In a separate experiment the water flux from the surface of Gila silt loam was determined in the same manner as the data in Table 3. Water flux was determined by weight loss of the soil dishes. The S.V.C. of water at 30 C is 31.3 mg/liter. Water flux was 4.80×10^5 and 7.00×10^5 μg cm^{-2} day^{-1} at 480 and 960 ml/min, respectively. This

Table 2. PESTICIDE VOLATILIZATION FROM TREATED SAND. SAND TREATED AT THE RATE OF 1000 μg/g. AIR FLOW WAS 480 ml min^{-1} (2.82 cm sec^{-1}) AT 30 C. EACH VALUE IS AN AVERAGE OF DUPLICATE DETERMINATIONS.

Pesticide	S.V.C.[1/] μg/l	Flux μg/cm^2/day	K_v[2/]
Trifluralin	4.29	31.0	132
Lindane	1.97	14.3	124
Dieldrin	0.202	1.23	119
p,p'-DDE	0.109	0.810	133
p,p'-DDT	0.0136	0.0924	128

[1/] Calculated from vapor pressure with the equation: $p = S.V.C.(RT/M)$. Values for the saturation vapor pressure were taken from Spencer and Cliath (1974), Spencer and Cliath (1972), Spencer and Cliath (1970), Spencer and Cliath (1969).

[2/] A proportionality factor calculated from the equation $f = K_v(S.V.C.)M^{-\frac{1}{2}}$.

Table 3. EFFECT OF AIR FLOW RATE ON PESTICIDE VOLATILIZATION FROM TREATED SAND AT 30 C. SAND TREATED AT RATE OF 1000 µg/g. EACH VALUE IS AN AVERAGE OF DUPLICATE DETERMINATIONS.

Pesticide	Air flow rate[1/] ml min^{-1}	Flux µg $cm^{-2}day^{-1}$	K_v
Lindane	120	4.96	42.9
Dieldrin	120	0.470	45.5
p,p'-DDE	120	0.303	49.7
p,p'-DDT	120	0.0362	50.1
Lindane	480	9.19	79.4
Dieldrin	480	0.990	95.7
p,p'-DDE	480	0.510	83.6
p,p'-DDT	480	0.0638	88.3
Lindane	960	14.2	123
Dieldrin	960	1.50	145
p,p'-DDE	960	1.07	175
p,p'-DDT	960	0.105	145

[1/] In the volatilization chamber used in this experiment, air flow rates of 120, 480 and 960 ml min^{-1} are equal to air flow velocities of 0.093, 0.374 and 0.748 cm sec^{-1}, respectively.

yielded K_v values of 61.5 and 89.7 for water flux at 480 and 960 ml/min air flow rate, respectively. These K_v values for water flux agree reasonably well with those determined for the pesticides. The agreement is especially good considering the differences in the S.V.C. and in the molecular weights of water and the pesticides.

These results indicate that pesticide volatilization of surface-applied pesticides can be adequately described by the relationship between the saturation vapor concentration of a pesticide and the constant K_v. The saturation vapor concentration or the vapor pressure of a pesticide is a readily determined laboratory value. The constant, K_v, would be evaluated through field calibration and testing. The results reported here show that a K_v calibrated for one compound or pesticide would be useful in predicting volatilization of other pesticides.

Pesticide treated sand simulates pesticide applications allowed to remain on a soil surface. The sand acts as an inert carrier for the pesticide exerting little adsorptive force on the pesticide. Interaction between a pesticide and soil results in adsorptive forces which may reduce the tendency for a pesticide to vaporize. Table 4 shows the influence of pesticide concentrations in Gila silt loam on volatilization rates. Pesticide volatilization increases with increasing concentration. This is in agreement with the results of Spencer et al. (1969). They have reported vapor phase sorption isotherms for dieldrin sorption by Gila silt loam. The equilibrium or saturation vapor concentration increased with increasing soil pesticide concentration reaching a maximum vapor density at approximately 30 µg/g soil pesticide concentration. Values of K_v have been calculated for dieldrin flux from Gila silt loam using the S.V.C. given by Spencer et al. for the appropriate dieldrin soil concentrations. Results are presented in Table 4. The pesticide flux and the K_v are seen to compare reasonably well with the values given in Table 3 for dieldrin flux at 480 ml min^{-1}. However, K_v increases at lower soil concentrations from 89.8 at 30 µg/g to 173 at 5 µg/g. This is apparently due to the decrease in vapor concentration in the air stream at 5 µg/g resulting in a greater vapor concentration gradient. This is similar to the effect of increased air flow rate in Table 3 resulting a greater rate of volatilization. The air flow rates used in these experiments are extremely low compared to wind speeds which would normally be encountered in field situations. Under field conditions with much greater wind speeds vapor concentration differences between different soil pesticide concentrations would be much less and the K_v values thus determined would doubtlessly be in better agreement.

Assuming the K_v determined for a soil dieldrin concentration of 5 µg/g is more representative of field conditions with higher wind velocities, than the fluxes measured from pesticide treated sand at 480 ml/min flow rate should be approximately doubled. Multiplying flux in $\mu g/cm^2$/day by 0.1 gives flux values in kg/ka/day. If a one kg/ha

Table 4. INITIAL DIELDRIN VOLATILIZATION RATES FROM TREATED GILA SILT LOAM AT 480 ml min^{-1} (0.374 cm sec^{-1}), 30 C, 10% GRAVIMETRIC SOIL WATER CONTENT AND 100% RELATIVE HUMIDITY.

Soil Concentration µg/g	S.V.C.[1/] µg/l	Flux µg/cm^2/day	K_v
5	0.030	0.265	173
10	0.073	0.545	146
30	0.190	0.870	89.8

[1/] Saturation vapor concentrations obtained from Spencer et al. (1969)

application of dieldrin were surface applied and left unincorporated, 10-20% could be lost in one day due to volatilization alone.

DIFFUSION BASED MODEL FOR SOIL INCORPORATED PESTICIDES

A comparison will be made between calculated results from our equations and results of published volatilization experiments. All these experiments, using lindane and dieldrin, were designed to measure the volatilization of pesticides from the surface of a soil column by leading an air stream over the surface. To prevent net loss of soil water and thus prevent transport of pesticide by mass flow to the soil surface, the air was brought to 100% relative humidity. The amount of pesticide carried by the air stream was measured for distinct periods of time.

The rate of volatilization of dieldrin measured by Spencer and Cliath (1973) is presented in Fig. 1. The soil was Gila silt loam at a bulk density of 1.4 g/cm^3. The initial concentration, C_o, in the soil was 1.4×10^4 ng/cm^3 (10 ppm). Soil water content was maintained at 23% (w/w). The temperature was kept at 30 C. Igue (1969) gives an apparent diffusion coefficient of D = 2.3 mm^2/week for dieldrin under these conditions. Air flow velocity was maintained at 2.15 cm sec^{-1}. The depth of the column was 11 cm. According to the evaluations given for Model II_1 we may assume the column to be infinite in length for at least 2×10^3 days after the start of the experiment. The solid curve in Fig. 1 was calculated according to equation [10]. The good agreement between measured and calculated values indicate that zero concentration at the soil surface is, under these conditions, a reasonable assumption. For very short times after the start of volatilization, the boundary conditions are violated in that the pesticide concentration at the soil surface is greater than zero. This may lead to some over estimation of the initial volatility rates. The low initial measured flux as compared to the calculated flux may be due to the experimental technique (e.g. losses by adsorption on walls).

Figure 2 represents data taken from a volatilization experiment carried out with lindane by Farmer et al. (1972). Parameters for this experiment were: Gila silt loam, soil water content 10% (w/w), bulk density 0.75 g/cm^3, temperature 30 C, initial concentration 7.5×10^2 ng/cm^3 (10 ppm), and depth of the column 0.5 cm. With the diffusion coefficient for lindane under these conditions equal to D = 30 mm^2/week (taken from Ehlers et al., 1969), we calculate that after 22 hours from the start of the experiment the concentration at the bottom of the column decreases by more than 1%. This accounts for the considerable difference between the two solid curves in Fig. 2, calculated from Model I and Model II.

Figure 2 also shows a curve calculated from Model IV. The air velocity across the surface of the column was v = 0.433 cm sec^{-1}. R was calculated from the adsorption isotherms given by Spencer and Cliath (1970), to be $R = 3 \times 10^{-5}$. Therefore h = R v/D becomes equal

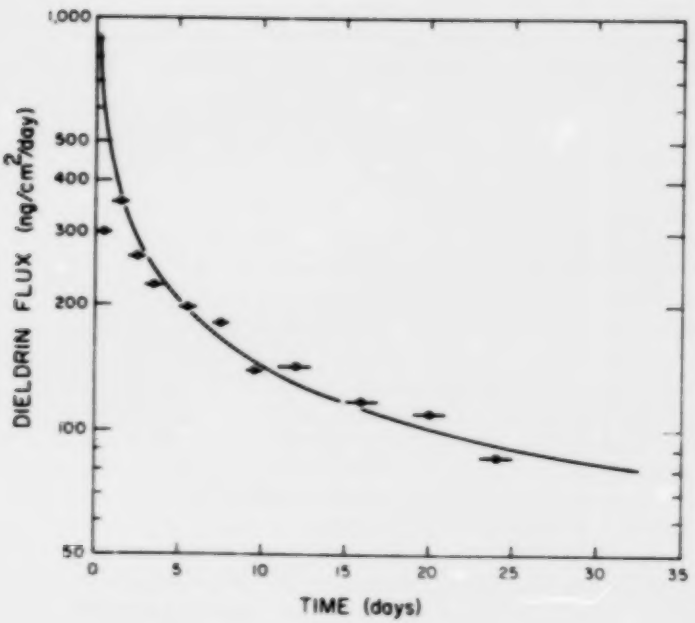

Fig. 1. Comparison between calculated values (solid curve) from Model II and experimental values (horizontal lines) for dieldrin flux. The experimental values were taken from Spencer and Cliath (1973). The length of the horizontal lines indicate the time over which the experimental values were taken.

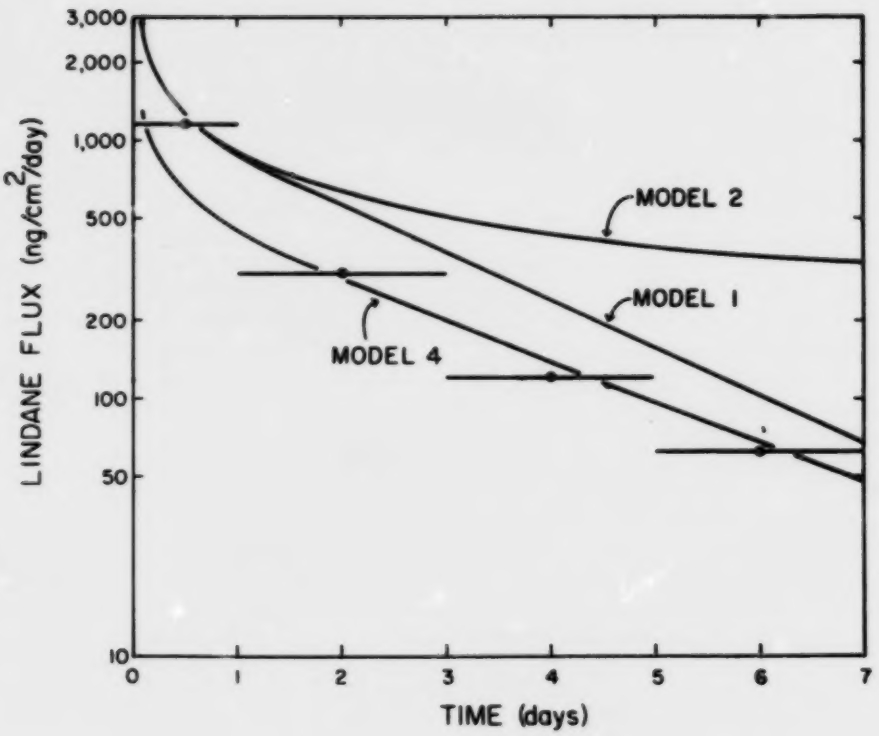

Fig. 2. Comparison between calculated and experimental values for lindane flux from treated Gila silt loam. Experimental data are from Farmer et al. (1972).

to 26.1 cm^{-1} compared to $k = R = 3 \times 10^{-5}$, the equations [19], [20], and [21] being applicable. The agreement between values calculated from Model IV and the measured values is quite good at the longer times and indicates that the flow velocity was not sufficient to create a zero concentration at the surface.

Volatilization experiments were conducted with dieldrin by Farmer et al. (1972), in which different air velocities were used. The soil was a Gila silt loam, soil water content 10% (w/w), bulk density 0.75 g/cm^3, initial dieldrin concentration was 7.5×10^3 ng/cm^3 (10 ppm), depth of the column was 0.5 cm, and temperature was kept at 20 C. The diffusion coefficient of 1.5 mm^2/week was derived from Igue (1969), assuming a reduction of 50% compared to the value given by this author to account for the lower temperature (20 C instead of 30 C). A similar reduction with decreasing temperature was found by Ehlers et al. (1969) for lindane. R was taken from Spencer, Cliath and Farmer (1969) to be 2.4×10^{-6}. With air velocities of 0.433 and 0.108 cm sec^{-1}, h became 39.46 and 9.86 cm^{-1}, respectively. Again, equations [19], [20], and [21] apply to this situation to allow calculation of pesticide flux.

Figure 3 shows the measured rates of dieldrin volatilization at two different air velocities together with the curves calculated from Model IV as well as a curve calculated for Model II. It can be seen, that under the conditions given in the experiment, at the higher air flow velocity the boundary condition "zero concentration at the soil surface" is appropriate. This is not true for the lower air flow velocity, where Model IV better accounts for the lower volatilization rates.

Note that the calculated curves for Model II and Model IV at the higher air velocity are very similar. Model IV predicts a lower flux during the initial time period than Model II. This is reasonable because initially there is pesticide at the soil surface and a higher air velocity would be necessary to maintain a concentration equal to zero at the surface which is required by Model II. As time progresses and volatilization has occurred, the surface is depleted of pesticide and the surface concentration can be kept at zero with a lower air velocity. The low fluxes measured, compared to the calculated, in the beginning of the experiment are probably due in part to losses by adsorption on walls.

From the equations presented for Model I and II, it can be seen that for a given initial concentration and depth of the soil layer, the flux at any time depends only on the apparent diffusion coefficient. Since the apparent diffusion coefficient depends on various parameters including bulk density, water content, concentration, temperature, and adsorption (Ehlers et al., 1969; Farmer and Jensen, 1970), all equations presented can only be used if during the time of observation, D remains constant. Ehlers et al., (1969) showed for lindane that this assumption holds true up to concentrations of about 20 ppm. This agreement

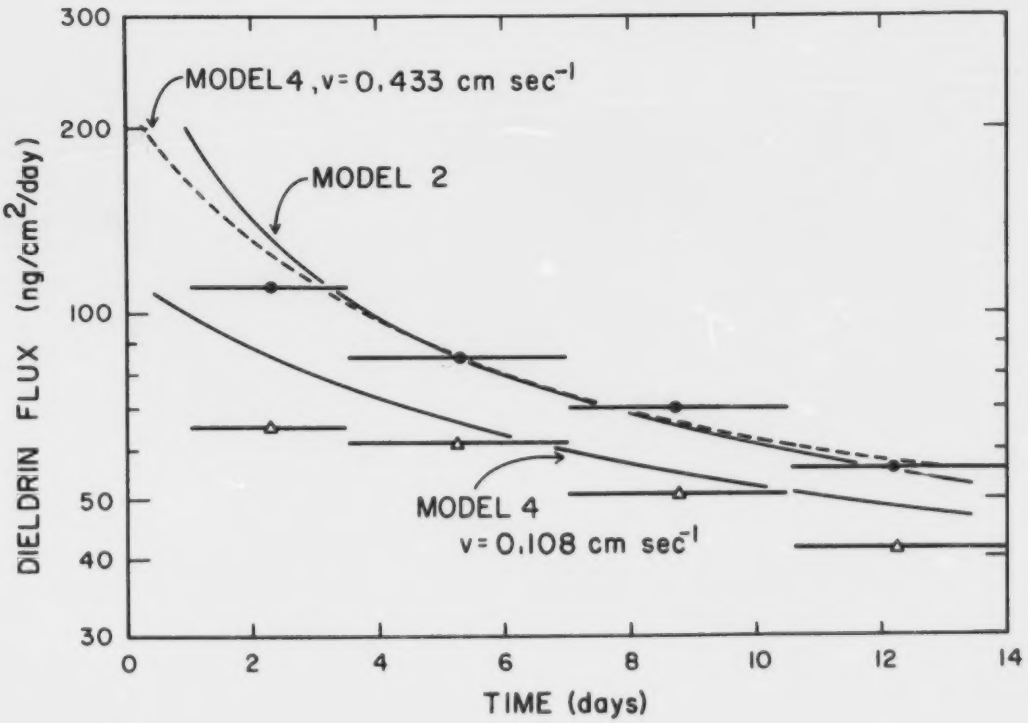

Fig. 3. Comparison of calculated and experimental values for dieldrin volatilization flux from uniformally treated Gila silt loam for air moving over the soil surface at two velocities. Experimental data from Farmer et al. (1972).

between measured and calculated pesticide fluxes, if an appropriate model is chosen, indicates that constancy for the conditions met in the experiments may also be assumed for the dieldrin diffuse coefficient.

Models I, II, and IV prove to be valid for describing volatilization losses from experiments carried out in the laboratory with appropriate boundary conditions. Prediction of volatilization rates of pesticides under field conditions with these or similar models become more difficult, mainly because the boundary conditions are not as well defined as in a laboratory experiment. Yet, the models are valuable at least in making reasonable estimates of pesticide losses of diffusion.

Let us take, for example, a pesticide incorporated in a soil surface layer. If the soil surface is in contact with a moving layer of air, and if diffusion to the surface is the only transport mechanism for pesticide in the soil, then Model IV should apply. The wind velocity can be measured as required for the model. One difficulty is that the model assumes that the air increment passing over each unit area of surface is initially devoid of pesticide. When a large land area is treated with pesticide, the wind will become enriched with pesticide as it passes over the field.

The results presented in Figures 1 and 3 indicate that only very low wind velocities (less than about 0.04 mi/hr^{-1} or 0.016 km/hr) are required to keep the pesticide concentration at zero at the soil surface. Thus it would appear that Models I, II, or III could be used with considerable confidence if there is much air movement.

The situation is different if we have a non-moving air layer above the surface, for example where the air movement is restricted by a standing crop. Under these conditions Model V applies.

Figure 4 gives some lindane flux curves calculated for different values of h. The diffusion coefficient D' for lindane in air is not known, but may be derived [Ehlers, et al. (1969), p. 502, equation (9)] as being 10^3 cm^2/day. The initial concentration was assumed to be 10^4 ng/cm^3, the diffusion coefficient for lindane in the soil 20 mm^2/week, R as used above was 3×10^{-5}. The depth of the soil layer treated with pesticide was assumed to be 10 cm. Equation [23] then gives the values of h which correspond with different values of d, the thickness of the air layer.

From Figure 4 it can be seen that a non-moving air layer may restrict the rate of volatilization considerably. Finally it may be mentioned that since we have under most conditions water movement in the soil profile, the models presented above predict volatilization rates from a soil surface better for moderately to strongly adsorbed pesticides of low mobility with moving water.

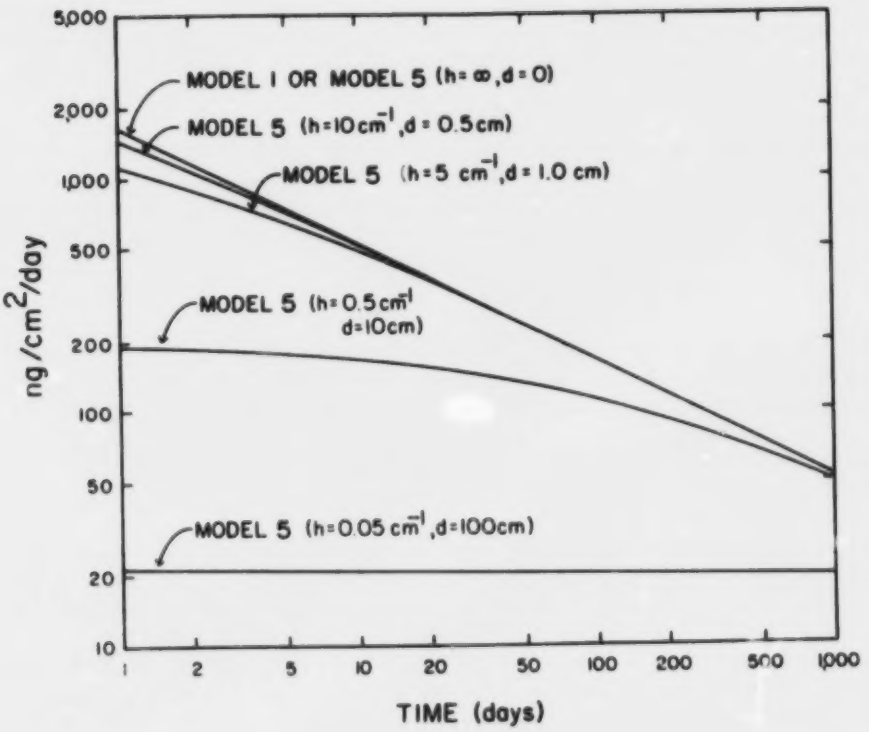

Figure 4. Calculated values for the influence of depth of non-moving air layer on lindane volatility flux from uniformally treated Gila silt loam.

MODEL BASED ON DIFFUSION AND MASS FLOW OF SOIL-INCORPORATED PESTICIDES

The combined diffusion and mass flow model for predicting volatilization from soil-incorporated pesticides was simulated using lindane in a column of Gila silt loam. The soil column used for the simulation was assumed to be 30 cm long with the top 10 cm uniformally treated with lindane at 10 μg/g (13.1 g/cc). This soil and pesticide were chosen for the simulation because of the information available on the diffusion, mass flow, adsorption, and volatilization of lindane in Gila silt loam. The data on column length, soil water content and soil bulk density assumed for the simulation were chosen to match the experimental conditions used for determining water conductivity in Gila silt loam. Soil water content was initially nearly uniform ranging from 0.382 g/cc at the top of the column to 0.392 g/cc at the 30 cm depth. Soil bulk density was 1.31 g/cc.

Sample input data for lindane diffusion coefficients are presented in Table 5. The data for lindane diffusion coefficients were taken from Shearer et al. (1973). The data were corrected to a temperature of 23 C by dividing the coefficients at 30 C by two. This correction factor was based on the temperature dependency of lindane diffusion developed by Ehlers et al. (1969).

The input data for water content, hydraulic head and soil water conductivity are presented in Table 6. This data was developed for water evaporation from Gila silt loam as a part of this project.

Adsorption data for lindane on Gila silt loam was taken from Huggenberger, Letey and Farmer, 1972.

The simulation was run for a one hundred day period assuming no rainfall events. A sample output data for 2.45 days after the start of volatilization is shown in Table 7. The pesticide flux through the top of the soil column as a function of time is shown in Table 8. For the experimental conditions chosen here the units of pesticide mass will be μg and the units of lindane flux will be $\mu g\ cm^{-2}\ day^{-1}$. From the data in Table 8, volatilization is seen to drop rapidly from an initial value of 2.7 $\mu g\ cm^{-2}$ to less than 0.5 $\mu g\ cm^{-2}\ day^{-1}$ in the first 3.5 days. The rate of volatilization levels off after the first few days. Between 31 and 35 days the flux has dropped to 0.012 $\mu g\ cm^{-2}\ day^{-1}$. Comparison of these rates of volatilization with those of Spencer and Cliath (1973) shows reasonable agreement between both the magnitudes of volatilization rates and the changes in rates with time. The conditions of Spencer and Cliath (1973) are different from the present in that water was being supplied continuously to the bottom of the soil column. In the present simulation there was no water movement across the 30 cm soil depth. However, the data of Spencer and Cliath (1973) is for lindane volatilization from Gila silt loam with both diffusion and mass flow operating. Their's is the only such data presently available under controlled conditions. The data of Spencer and Cliath (1973) does provide partial confirmation of the predictive model

Table 5. SAMPUS INPUT DATA. EXPERIMENTAL VALUES OF APPARENT DIFFUSION COEFFICIENTS (D_{vs}) WITH CORRESPONDING WATER CONTENT VALUES (θ). DATA TAKEN FOR THE PESTICIDE LINDANE (SHEARER ET AL., 1973).

D_{vs} $cm^2\ day^{-1} \times 10^2$	θ $cm^3\ cm^{-3} \times 10^2$
0.0	0.0
0.0	1.96
0.0	2.62
0.0	3.67
1.57	5.90
1.36	11.8
1.25	19.6
1.18	26.2
0.857	33.4
0.772	38.0
0.772	44.5
0.772	51.0

Table 6. SAMPLE INPUT DATA. SOIL WATER CONTENT, WATER CONDUCTIVITY, AND WATER CAPACITY AS A FUNCTION OF THE PRESSURE HEAD.

ITER. NO. 3 NO. OF POINTS NOT PASSING TEST 0 30 TIME STEP TIME 2.4700 00 DAY. DELTA TIME 1.152D-01 DAY.

TIME IS 5.929D 01 HOURS OR 2.4700 00 DAYS FLUX OUT 3.406D-15 CM/DAY. CUMULATIVE OUTFLOW FROM FLUX 1.990D 00 CM
CUMULATIVE OUTFLOW FROM THETA PROFILE 1.674D 00 CM NO. OF TIMES OVERITERATED 0 FLUX BY CUMULATIVE DIFF. 6.244D-01
Q/QINF. BY INTEGRAL 1.596D-01 Q/QINF. BY DIFFERENCE 1.694D-01 AVE. K AT SURFACE 2.936D-02 FLUX AT SURFACE 8.431D-01
AMOUNT IN PROFILE AT THIS TIME 9.870D 00 CM FLUID APPLIED AT Z=0 TO THIS TIME 0.0 CM NET GAIN OR LOSS BY FLUX 0.0 CM

Z	PRESSURE HEAD	WATER CONTENT	HYD. HEAD	PORE VEL.	Z	PRESSURE HEAD	WATER CONTENT	HYD. HEAD	PORE VEL.
-2.900D 01	-3.730D 02	3.501D-01	-4.020D 02	5.794D-02	-1.400D 01	-4.215D 02	3.322D-01	-4.359D 02	1.196D 00
-2.700D 01	-3.758D 02	3.490D-01	-4.048D 02	1.974D-01	-1.200D 01	-4.351D 02	3.283D-01	-4.471D 02	1.370D 00
-2.500D 01	-3.794D 02	3.474D-01	-4.084D 02	3.439D-01	-1.000D 01	-4.507D 02	3.237D-01	-4.607D 02	1.553D 00
-2.300D 01	-3.841D 02	3.455D-01	-4.131D 02	4.926D-01	-8.000D 00	-4.696D 02	3.181D-01	-4.776D 02	1.753D 00
-2.100D 01	-3.899D 02	3.430D-01	-4.189D 02	6.447D-01	-6.000D 00	-4.932D 02	3.111D-01	-4.992D 02	1.954D 00
-1.900D 01	-3.970D 02	3.400D-01	-4.260D 02	7.992D-01	-4.000D 00	-5.236D 02	3.038D-01	-5.276D 02	2.154D 00
-1.700D 01	-4.057D 02	3.370D-01	-4.347D 02	9.514D-01	-2.000D 00	-5.622D 02	2.952D-01	-5.642D 02	2.475D 00
-1.500D 01	-4.160D 02	3.340D-01	-4.450D 02	1.112D 00	0.0	-6.148D 02	2.842D-01	-6.148D 02	2.966D 00

Z CM	C	S MASS/GM SOIL	C + S	CL MASS/CC(LIQ)	C	S MASS/CC(TOTAL)	C + S	SM MASS/GM	DVS CM2/DAY
-1.200D 01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.824D-03
-1.100D 01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.923D-03
-1.000D 01	5.596D-01	7.919D 00	8.478D 00	2.265D 00	7.330D-01	1.037D 01	1.111D 01	9.066D 00	9.031D-03
-9.000D 00	7.398D-01	8.899D 00	9.638D 00	3.019D 00	9.692D-01	1.166D 01	1.263D 01	9.069D 00	9.149D-03
-8.000D 00	7.638D-01	9.044D 00	9.808D 00	3.145D 00	1.001D 00	1.185D 01	1.286D 01	9.061D 00	9.280D-03
-7.000D 00	7.591D-01	9.043D 00	9.622D 00	3.159D 00	9.944D-01	1.187D 01	1.287D 01	9.063D 00	9.427D-03
-6.000D 00	7.510D-01	9.065D 00	9.816D 00	3.162D 00	9.838D-01	1.188D 01	1.286D 01	9.065D 00	9.593D-03
-5.000D 00	7.417D-01	9.067D 00	9.809D 00	3.160D 00	9.716D-01	1.188D 01	1.285D 01	9.068D 00	9.757D-03
-4.000D 00	7.329D-01	9.066D 00	9.799D 00	3.160D 00	9.601D-01	1.188D 01	1.284D 01	9.069D 00	9.917D-03
-3.000D 00	7.235D-01	9.089D 00	9.812D 00	3.161D 00	9.478D-01	1.191D 01	1.285D 01	9.069D 00	1.010D-02
-2.000D 00	6.858D-01	8.931D 00	9.617D 00	3.043D 00	8.984D-01	1.170D 01	1.260D 01	9.078D 00	1.030D-02
-1.000D 00	6.391D-01	1.090D 01	1.174D 01	3.792D 00	1.099D 00	1.428D 01	1.538D 01	1.090D 01	1.054D-02
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.079D-02

TRANSFER OF MATERIAL-MASS/SQ CM/DAY

Z	DIFFUSION	BY WATER	TOTAL	CONC. GRAD	Z	DIFFUSION	BY WATER	TOTAL	CONC. GRAD
-1.20D 01	-1.714D-02	0.0	-1.714D-02	2.221D 00	-6.00D 00	3.972D-05	1.922D 00	1.922D 00	-4.212D-03
-1.10D 01	-3.203D-02	0.0	-3.203D-02	3.636D 00	-5.00D 00	4.561D-05	2.003D 00	2.003D 00	-4.753D-03
-1.00D 01	-3.415D-02	1.138D 00	1.104D 00	3.832D 00	-4.00D 00	5.057D-04	2.106D 00	2.107D 00	-5.180D-02
-9.00D 00	-2.479D-02	1.600D 00	1.575D 00	2.747D 00	-3.00D 00	-4.794D-03	2.213D 00	2.208D 00	4.826D-01
-8.00D 00	-3.425D-03	1.754D 00	1.751D 00	3.746D-01	-2.00D 00	-1.258D-02	2.223D 00	2.211D 00	1.242D 00
-7.00D 00	-4.247D-04	1.846D 00	1.846D 00	4.576D-02	-1.00D 00	-2.069D-02	2.805D 00	2.785D 00	2.002D 00
-6.00D 00	3.972D-05	1.922D 00	1.922D 00	-4.212D-03	0.0	2.588D-01	0.0	2.588D-01	-2.446D 01

MASS/CM2 SOIL TRANSFERRED FROM SOLUTION PHASE 2.695D 00
MASS/CM2 SOIL TRANSFERRED FROM ADSORBED PHASE 1.822D 00
TOTAL MASS/CM2 SOIL VOLATILIZED 4.517D 00
FRACTION VOLATILIZED 3.448D-02
MASS/CM2 SOIL IN SOLUTION 9.442D 00 MASS/CM2 SOIL ADSORBED 1.170D 02 TOTAL MASS/CM2 SOIL 1.265D 02

ITER. NO. 3 NO. OF POINTS NOT PASSING TEST 0
AMOUNT DOWNWARD PAST Z= -10 CM. 6.345D-03

Table 7. SAMPLE OUTPUT DATA. WATER RELATIONS AND PESTICIDE DISTRIBUTION IN SOIL COLUMN 2.1 DAYS AFTER INITIATION OF PESTICIDE VOLATILIZATION.

HEAD CM	THETA CM/CM	CONDUCTIVITY CM/DAY	CAPACITY 1/CM	HEAD CM	THETA CM/CM	CONDUCTIVITY CM/DAY	CAPACITY 1/CM
-5.4000 01	4.9000-01	3.7500 00	2.9000-04	-1.0000 02	4.7500-01	1.2150 00	2.9000-04
-2.0000 02	4.5010-01	6.1210-01	4.9000-04	-3.0000 02	3.8110-01	1.9440-01	5.2090-04
-4.0000 02	3.3870-01	8.6150-02	3.4720-04	-5.0000 02	3.0910-01	4.5820-02	2.5350-04
-6.0000 02	2.8680-01	2.7360-02	1.9600-04	-7.0000 02	2.6930-01	1.7690-02	1.5770-04
-8.0000 02	2.5490-01	1.2120-02	1.3060-04	-9.0000 02	2.4290-01	8.6900-03	1.1070-04
-1.0000 03	2.3260-01	6.4490-03	9.5390-05	-2.0000 03	1.8050-01	9.0750-04	2.9050-05
-3.0000 03	1.5840-01	2.6820-04	1.6700-05	-5.0000 03	1.3440-01	6.7930-05	8.6520-06
-7.5000 03	1.1790-01	2.1570-05	5.0620-06	-1.0000 04	1.0750-01	9.5600-06	3.4610-06
-1.5000 04	9.4320-02	3.0360-06	2.0250-06	-2.0000 04	8.5980-02	1.3450-06	1.3840-06
-2.5000 04	8.0020-02	7.1520-07	1.0310-06	-3.0000 04	7.5450-02	4.2720-07	8.3690-07
-3.5000 04	7.1800-02	2.7620-07	6.6060-07	-4.0000 04	6.8780-02	1.8930-07	5.5370-07
-5.0000 04	6.4000-02	1.0620-07	4.1220-07	-1.0000 05	5.1210-02	1.0540-07	1.3500-07
-3.1620 05	4.0400-02	9.1310-08	2.6240-08	-1.4650 06	2.9500-02	4.3280-08	4.1360-09

Table 8. SAMPLE OUTPUT DATA. PESTICIDE VOLATILIZATION FLUX THROUGH THE TOP OF THE SOIL COLUMN AS A FUNCTION OF TIME AFTER INITIATION OF VOLATILIZATION.

TIME(DAYS)	MASS/SQ CM	MASS/SQ CM/DAY	TIME(DAYS)	MASS/SQ CM	MASS/SQ CM/DAY	TIME(DAYS)	MASS/SQ CM	MASS/SQ CM/DAY
0.0	1.310D 02	-2.676D 00	1.318D 00	1.266D 02	-1.765D 00	2.470D 00	1.265D 02	-9.695D-01
3.622D 00	1.260D 02	-4.627D-01	4.774D 00	1.253D 02	-6.151D-01	6.733D 00	1.238D 02	-6.149D-01
9.037D 00	1.224D 02	-3.853D-01	1.318D 01	1.224D 02	-2.889D-01	2.010D 01	1.194D 02	-2.560D-01
2.563D 01	1.181D 02	-2.051D-01	3.126D 01	1.173D 02	-7.844D-02	3.500D 01	1.171D 02	5.553D-03

developed in this project.

This model has been run several times varying the values for the diffusion coefficient and the coefficient for the adsorption of the pesticide by the soil. This would simulate the volatilization of pesticides from various pesticide-soil combinations. As expected the rates of pesticide volatilization decreased when either the diffusion coefficient decreased or the adsorption coefficient increased.

Field testing of this model is needed to test its validity and to determine under what conditions it may or may not be applicable. However, several recommendations can be suggested as to when this model may be applicable or when other models discussed in this text should be tried as an alternative.

The combined diffusion and mass flow model would be expected to be applicable under conditions when wind speed and turbulence are sufficient to maintain nearly zero pesticide vapor concentration in the air at the soil surface. As discussed with the diffusion based model, the results presented in Figures 1 and 3 indicate only very low wind velocities (less than about 0.016 km/hr) are required to keep dieldrin concentration essentially zero at the soil surface.

The combined diffusion and mass flow model as presented here would not be expected to apply with a non-moving air layer above the soil as, for example, when air movement is restricted by a crop cover. Additional development of the model would require replacing the boundary condition of zero concentration at the soil surface with one similar to that developed for Model V of the diffusion based model to be applicable with a crop cover present. Figure 4 shows that the layer of non-moving air does not have to be very thick before having a considerable effect on the volatilization rate.

Another situation not accounted for in the combined model in its present state is the redistribution of a pesticide in the soil which may take place after a rainfall event. The model begins with initially uniform soil concentration. This is probably reasonable for a compound that is well incorporated at the time of application. However, if the pesticide is mobile in moving water, its redistribution in the soil profile after water is added will depend on both the amount and intensity of the event.

It should be noted that from the nature of the input data in Table 4, volatilization will be nearly always zero from a dry soil (less than about 100 bars). Most non-polar or weakly polar pesticides will be strongly adsorbed by dry soils. Any mobile pesticide that is moved up to the soil surface as water evaporates will be adsorbed at the surface. This adsorbed pesticide will doubtlessly go off in a burst of volatilization when the soil is rewetted so that over a long time average the rate of volatilization may be the same whether the soil is continuously wet or going through wetting and drying cycles.

This assumes, of course, negligible irreversible adsorption during the drying cycle.

For strongly adsorbed, immobile pesticides, such as trifluralin, the mass flow component will be essentially zero in the combined diffusion and mass flow model. For these compounds, the diffusion based models will probably prove very useful. For trifluralin the mass flow component can be ignored and the diffusion based models utilized. Bode et al. (1973a, 1973b) have determined the influence of various soil and environmental factors on the diffusion coefficient of trifluralin. These workers used the methods of Ehlers et al. (1969a, 1969b) for investigations which provides the type of data required by the diffusion based models.

The most significant input data for all of the models presented here are soil pesticide concentrations. Actually reasonable estimates could doubtlessly be made of pesticide volatilization rates using the model based on surface applied pesticides if frequent data were available on concentrations at the soil surface. Many situations could be treated as surface-applied when information is available on the relationship between vapor density and soil concentrations such as that Spencer and his coworkers have developed for dieldrin, lindane, DDT and trifluralin (Spencer, Cliath and Farmer, 1969; Spencer and Cliath, 1970; Spencer and Cliath, 1972; Spencer and Cliath, 1974). For this model, the only data necessary are the pesticide vapor densities and the volatilization rate for a reference compound under similar conditions. Excellent agreement was obtained in this project for the K_v values of a number of compounds under different conditions. The factor, K_v, takes into account many field variables that would be difficult to obtain independently.

As noted above Spencer and coworkers have developed considerable data on the vapor sorption isotherms for a number of pesticides on soil. Furthermore, Spencer et al. have shown a strong negative correlation between soil organic matter and vapor density for dieldrin (Spencer, Farmer, and Cliath, 1973) and for trifluralin (Spencer and Cliath, 1974). The vapor density of soil-applied pesticide decreased with increasing organic matter of several soils even though the clay content was often inversely related to the organic matter content. Using information of this kind it should be possible to make reasonable estimates of pesticide vapor densities on soils without having to determine vapor sorption isotherms on every soil.

EFFECT OF TEMPERATURE GRADIENT ON PESTICIDE MOVEMENT

The initial conditions of the soil columns are given in Table 9. To be able to understand the distribution of the pesticides as shown in Figures 5, 6, and 7 the transfer of water in the liquid and vapor phase in the three experiments is analyzed first. Table 10 shows the parameters necessary to characterize water transfer in these experiments. The parameters are the average suction head, h, the suction gradient along the column at steady state, ∇h, the average temperature, T, and the temperature gradient along the columns, ∇T. Taking the distance x increasing from the warm to the cold end results in negative values for the gradients.

It has to be pointed out here, that due to a leak at the warm end of the columns 2 and 3 they cannot be considered closed systems. Steady state water transfer as discussed earlier did therefore not occur in these two columns. The suction values and suction gradients reported in Table 9 for these columns are average values taken over the whole duration of the experiments. The water loss as measured as difference between the weight at the beginning and end of the experiments was 1.1% and 1.8% for columns 2 and 3 respectively, based on the total oven-dry weight of the soil in the columns. No weight loss was recorded for column 1. Since in all experiments the columns were sealed with equal care, it has to be concluded that while the sealant was adequate for the lower temperature and vapor pressure of column 1, it was not sufficient to completely seal off the columns at the higher temperatures of columns 2 and 3.

L_w is the transmission coefficient for liquid water as used in Darcy's law:

$$J_w = L_w \nabla h \qquad [40]$$

where J_w is the flux of liquid water. L_w was calculated from the following water conductivity functions:

For Gila silt loam:

$$L_w = 2.6 \times 10^{4} \, h^{-2.80} \qquad [41]$$

and Pachappa sandy loam:

$$L_w = 8.5 \times 10^{6} \, h^{-4.52} \qquad [42]$$

Table 9. INITIAL CONDITIONS OF SOIL COLUMNS

Experiment	Pesticide	Soil	θ cm^3/cm^3	P_w %	h_o cm	C_o ppm
1	Lindane	Gila silt loam	1.26	21.0	388.6	10.0
2	Diuron	Pachappa sandy loam	1.61	15.0	70.0	5.0
3	Atrazine	Pachappa sandy loam	1.61	15.0	70.0	5.0

Table 10. PARAMETERS CHARACTERIZING WATER FLUX IN SOIL COLUMNS

Experiment	h cm	∇h cm/cm	T C	∇T C/cm	L_w cm/hr x 10^3	L_v cm^2/C hr x 10^3	J_w cm x 10^5	J_v cm x 10^5
1	395	-2.46	27.4	-0.38	1.45	4.0	-357	152
2	118	-0.30	41.4	-1.52	3.74	8.3	-112	1262
3	137	-0.57	44.2	-1.81	1.87	9.5	-105	1720

The conductivity functions were determined in separate experiments by the transient flow method as described by Weeks and Richards (1967). Equation [42] has been reported previously in a study by Weeks, Richards, and Letey (1968).

The transmission coefficient for water vapor L_v was obtained following the development of Letey (1968), and the flux of water vapor J_v calculated from the equation:

$$J_v = -L_v \nabla T \qquad [43]$$

Analyzing the liquid water and water vapor fluxes as given in Table 9, the following can be observed. The flux of liquid water is highest in column 1 followed by columns 2 and 3. Considering the longer duration of experiment 1 as opposed to 2 and 3, the total liquid water transfer in column 1 was therefore considerably greater than in columns 2 and 3. On the other hand, the flux of water vapor is greatest in column 3 followed by columns 2 and 1. As mentioned earlier, the fluxes of water vapor and liquid water should be equal at steady state in a closed system. The big differences between liquid water and water vapor fluxes as calculated for columns 2 and 3 can be explained by the fact that there was a leak at the warm end of these columns as mentioned earlier. Part of the water vapor generated at the warm end of the columns escaped out of the system and was not transferred to the cold end of the columns. Consequently, less water was available for liquid water transfer from the cold end to the warm end of the soil columns. The fact that the calculated water vapor flux in column 1 was smaller than the estimated liquid water flux can be explained as follows. The values of L_v were calculated using an average value of 3.0×10^{-3} cm^2 deg^{-1} hr^{-1} corrected for the average temperature of the experiments as suggested by Letey (1968). Letey (1968) points out however in his study that L_v increases with decreasing sand content of the soil. This average value of L_v could therefore be a low estimate for Gila silt loam, a soil with a small proportion of coarse particles.

The distribution of Cl^- ions at the end of the experiments is indicative of the transfer of liquid water. The Cl^- ion concentration is higher at the warm end than at the cold end as can be easily seen in Figures 2 and 3. This indicates a net liquid water transfer from the cold end to the warm end as expected. The position of the concentration minimum of the Cl^- ion can however not be readily explained assuming only unidirectional flow of liquid water. It has to be concluded that a small amount of liquid water was also transferred from the warm end to the cold end in experiments 2 and 3. Since the suction head was low in experiments 2 and 3 especially in the early stages of the experiments this observation is compatible with conclusions reached by Letey (1968) concerning liquid water transfer due to temperature gradients. The sharp increase in the Cl^- ion concentration at the warm end of the columns 2 and 3 also reflects the loss of water vapor at the end of the

columns and therefore a more rapid liquid water transfer at that end of the column than on the average over the whole columns. The moisture distributions leads to the same conclusions. In column 1 the moisture content is linearly increasing from the warm to the cold end of the column as expected in a closed system at steady state such as studied here. In columns 2 and 3 however the moisture content abruptly drops toward the warm end indicating a net water loss of the system at that end.

The distribution of lindane in column 1 (Figure 5) appears plausible from the introductory remarks on the expected pesticide transfer mechanisms involved in the system. Transfer of pesticide molecules in the solution phase from the cold to the warm end and transfer of pesticide molecules from the warm to the cold end in the vapor phase would let us expect a pesticide distribution at the warm end of the experiment as shown in Figure 5. It is interesting to note that the two concentration maxima occur at equal distances from the warm and the cold end respectively. This would seem to be an experimental indication of equal fluxes of the pesticide in the two directions. Transfer of the pesticide by diffusion due to a concentration gradient in the nonvapor phase is obviously smaller than the other two transport processes, since it would tend to equalize the concentration distribution as shown in Figure 1. The fact that only approximately 75% of the pesticide added was recovered in the final analysis is explained by losses during the sectioning of the column, adsorption of the pesticide on the walls of the columns and incomplete extraction of the pesticide from the soil samples. As pointed out earlier, the leak in columns 2 and 3 affected the water transfer characteristics of these columns to a degree which makes a direct comparison of the pesticide distributions of colums 2 and 3 with the pesticide distribution of column 1 difficult. Comparison of the distributions of the Cl^- ions and the respective pesticide distribution in Figures 6 and 7 shows a striking simularity between the respective curves. The minimal Cl^- ion concentration in column 3 is lower than the minimal Cl^- ion concentration in column 2. Accordingly the maximum concentration of atrazine in column 3 is lower than the minimum diuron concentration in column 2. The same relationship holds true for the concentration maxima of Cl^- ions and pesticides at the warm end of columns 2 and 3. From these results it would seem that the transfer of diuron and atrazine occurred mostly in the liquid phase as opposed to the experiment with lindane where equal amounts of pesticide molecules seemed to be transferred in the liquid and vapor phase.

Exact measurements for the different vapor densities in the soils at the given pesticide concentrations and moisture contents are not available. The vapor diffusion coefficients are also not known for all three pesticides in the soil systems under investigation. It is therefore not possible to exactly calculate the fluxes of pesticide vapor in the three experiments at this time. The fact that the vapor pressure of lindane in air is higher than the vapor pressures of diuron and atrazine at the temperatures existing in these experiments might however

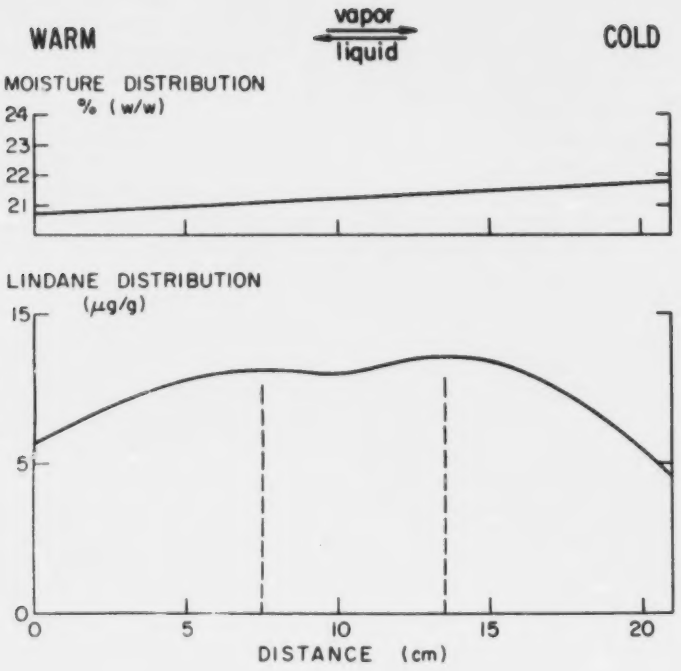

Figure 5. Effect of temperature gradient on the distribution of water and lindane in Gila silt loam.

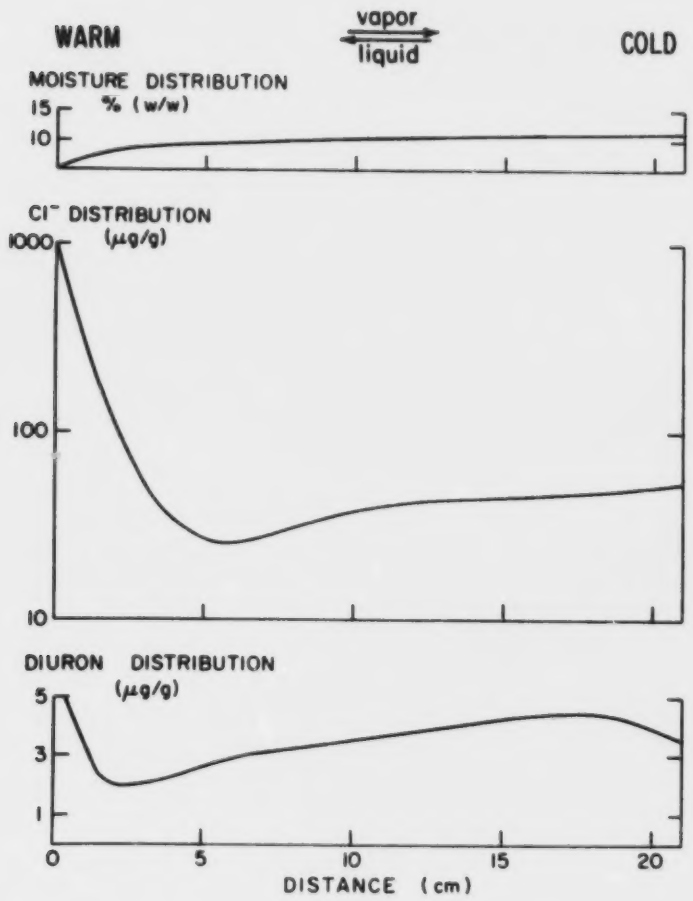

Figure 6. Effect of temperature gradient on the distribution of water, Cl^-, and diuron in Pachappa sandy loam.

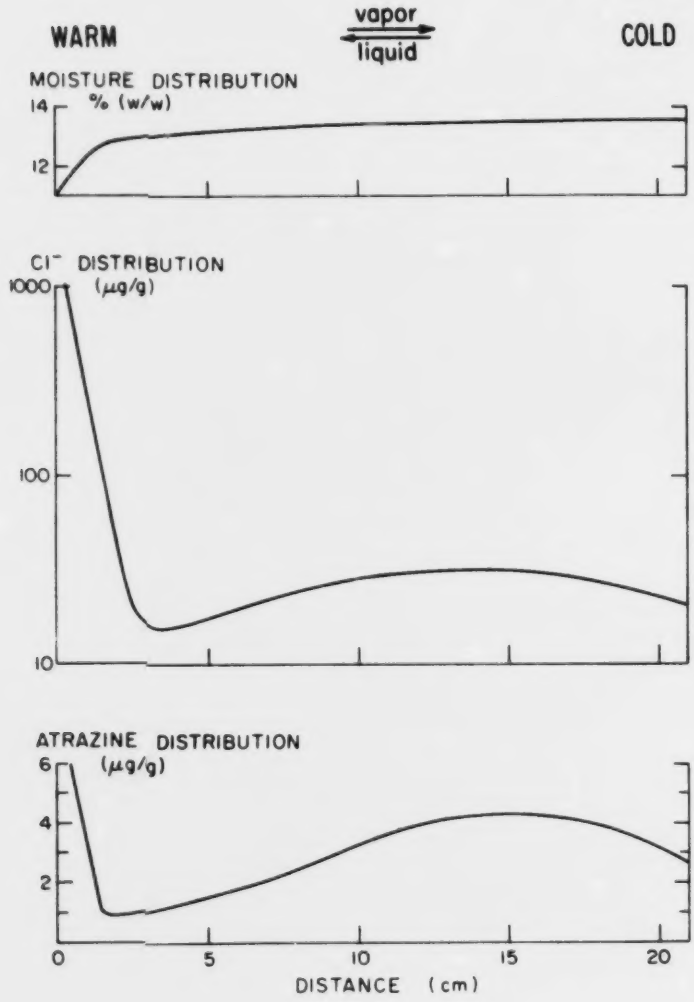

Figure 7. Effect of temperature gradient on the distribution of water, Cl^-, and atrazine in Pachappa sandy loam.

be a possible explanation. As discussed earlier in regard to water vapor loss at the warm end of columns 2 and 3, loss of pesticide vapor at the warm end of the columns could be another possible explanation for the concentration minima close to the warm end of the columns and little transfer of pesticide vapor to the cold end of the columns. The failure to recover the total amount of diuron and atrazine added to the columns is explained as above for column 1.

In summary it can be said that the system investigated offers interesting possibilities to study vapor diffusion and mass transfer of pesticides simultaneously. In order to calculate the resulting pesticide fluxes and to compare quantitatively the results of the experiments using different pesticide compounds, further measurements of properties of the pesticides in the given soil systems are necessary.

SECTION VIII

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SECTION IX

GLOSSARY

Definitions of Symbols Used in the Text.

q = rate of diffusion

K_1 = constant for geometry of the soil

ΔC_a = vapor concentration gradient

d = depth of air layer

K_2 = proportionality factor

K_v = proportionality factor between volatilization flux and the saturation vapor concentration

S.V.C. = saturation vapor concentration

R = molar gas constant

T = absolute temperature

K'_v = proportionality factor between volatilization flux and the vapor pressure

c, C = pesticide concentration in soil (g cm^{-3} total volume)

x, z = distance measured normal to the soil surface

t = time

L = depth of soil layer treated uniformally with pesticide

C_o = initial soil pesticide concentration (g cm^{-3})

f = pesticide flux through the soil surface

V = volume of air

v = air flow velocity

C_a = pesticide concentration in air

C_s = pesticide concentration at the soil surface

R = proportionality factor between C_a and C_s

D' = diffusion coefficient of pesticide in air

h = pressure head of water (cm)

$\theta(h)$ = volumetric water content as a function of the pressure head (cm^3 of water/cm^3 of total space)

$\partial\theta(h)/\partial h$ = specific water capacity

$K(h)$ = water conductivity as a function of the pressure head ($cm\ day^{-1}$)

h_o = initial pressure head

$D_{vs}(\theta)$ = total apparent diffusion coefficient as a function of $\theta(h)$

$V(\theta)$ = pore water velocity as a function of $\theta(h)$

C' = concentration in solution (mass cm^{-3})

ρ_b = soil bulk density ($g\ cm^{-3}$)

K = constant relating adsorbed and solution phase pesticide concentrations

S_{max} = maximum adsorbed phase concentration (mass/g soil)

N = ratio of the exponents for desorption to adsorption in the Freundlich equation for C'.

SECTION X

APPENDICES

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A.	Explanation of Symbols and Variables in Water Evaporation - Pesticide Volatilization Program.	58
B.	Computer Program - Model Based on Diffusion and Mass Flow of Soil-Incorporated Pesticides.	65

Appendix A. Explanation of Symbols and Variables in Water Evaporation-Pesticide Volatilization Program.

Input Parameters

1. Format Statement 998.

N - The number of intervals between upper and lower boundary.

ITMAX - The maximum number of iterations for any time step.

LPRTC - A print control variable. If LPRTC = 1, results are printed for every time step. If LPRTC = 5, for example, results are printed for every 5th time step. Results are printed for the first and last time step (if the problem is finished) regardless of the value of LPRTC.

NUMCØL - Can be used to return control at end of one problem to some point in main program to consider input data for other problems, etc.

EPSLØN - The values of the pressure head for the present iteration (HEADPI) are compared. If the absolute value of the difference between any pair of values exceeds EPSLØN, another iteration is performed, otherwise the solution of the problem proceeds.

EPSLNC - The values of the pesticide concentration (mass/unit volume of space (cm^3) for the present iteration (CØPPBS) and for the past iteration (CPBSPI) are compared. If the absolute value of the difference between any pair of values exceeds EPSLNC, another iteration is performed. If EPSLNC is not exceeded the solution continues.

$R = \Delta t/(\Delta Z)^2$, where Δt = interval between time steps (days), ΔZ = distance (cm) between space intervals. R initializes Δt and is used in solution.

DELTA1, DELTA2 - If the absolute values of the differences between present time concentration values (CØPPBS) and past time values (CPSPT) are less than DELTA1 for all points, Δt and R are doubled for the next time step. If the differences above exceed DELTA2, Δt and R are multiplied by 0.75 and results are recalculated for a new (smaller) step.

QFRACT - If the amount of water evaporated from the soil column or profile divided by the initial water content exceeds QFRACT, the calculations stop and results for the time step are printed.

CM - Length of column or depth of profile in cm.

TIMEMX - The maximum amount of time for evaporation to occur expressed in days.

2. Format Statement 997.

CØNMAT - Initial concentration of pesticide (mass/gm dry soil).

DEPTH - Depth of initial pesticide distribution in cm.

PB - Average bulk density of soil (gm soil/cm^3 space).

K - Adsorption constant (cc liquid/gm dry soil).

EXPØN - Exponent associated with K for desorption (assumed = 1 for adsorption).

NDVSPT - The number of paired values of the apparent diffusion coefficient and water content from experimental data.

IN - The number of points at which related experimental values of hydraulic conductivity, water content, water capacity, and pressure head are available.

3. Format Statement 995.

ACØNST - An empirical constant used in this study and related to the rate of change of water pressure of the soil surface.

4. Format Statement 978.

DVSIN - Apparent diffusion coefficient (cm^2/day).

THDSIN - Water content (cm^3 liquid/cm^3 space).

5. Format Statement 996.

HEAD - Pressure head (cm).

THETA - Water content (cm^3 liquid/cm^3 space).

HCØND - Water conductivity (cm/day).

CAP - Water capacity (cm^{-1}).

Other Variables in Dimension Statements of Main Program

HEADC - Pressure head values at the present time step.

HEADPT - Pressure head values at the end of the previous time step.

HEADPI - Initial pressure head values and pressure head values of each iteration within time steps.

CAPC - Water capacity values at the present time step.

CAPP - Water capacity values at the end of the previous time step.

CØNC - Water conductivity values at the end of the present time step.

CØNP - Water content values at the end of the previous time step.

THETAC - Water content values at the present time step.

HYHEAD - Hydraulic head (cm) at the present time step.

HYGRAD - Hydraulic gradient values at the present time step.

HYHDPT - Used to store initial pressure head values.

Z - Vertical distance (cm), positive upward.

C - Concentration of pesticide in solution (mass/gm dry soil) at present time step.

CL - Concentration of pesticide in solution (mass/cm^3 space) at present time step.

CTHEPT - Concentration of pesticide in solution (mass/cm^3 space) at end of previous time step.

CTHEPI - Concentration of pesticide in solution (mass/cm^3 space) at each iteration within time steps.

S - Concentration of adsorbed pesticide (mass/gm dry soil) at present time step.

SMAX - Maximum value of S obtained at any position (Z).

PBSC - Concentration of adsorbed pesticide (mass/cm^3 space) at present time step.

PBSPT - Concentration of adsorbed pesticide (mass/cm^3 space) at end of previous time step.

CØPPBS - Total concentration of pesticide, adsorbed plus solution phases, (mass/cm^3 space) at present time step.

CPSPT - Total concentration of pesticide (mass/cm^3 space) at end of previous time step.

CPBSPI - Total concentration of pesticide (mass/cm^3 space) at each iteration.

CGRAD - Total concentration gradient (mass/cm^4 space) at present time step.

CPLUSS - Total concentration of pesticide (mass/gm dry soil; C + S.

THETPT - Initial water content (THETAC) values stored.

DV - Initial water conductivity (CØNC) values stored.

DVPT - Initial water capacity (CAPC) values stored.

DVIN - Apparent diffusion coefficient values from input data stored.

DVS - Apparent diffusion coefficient values at present time step.

DVSPT - Apparent diffusion coefficient values at end of previous time step.

PØREV - Average liquid velocity in pores (cm/day).

ETIME - Elapsed time values (days).

TØTMAT - Total amount of pesticide in profile (mass/cm^2 space).

FLXMAT - Rate of pesticide movement of surface (mass/cm^2/day).

ABLCK, BBLCK, CBLCK - Coefficients of equations (diagonals) used in tridiagonal matrix.

HBLCK - Right hand side of solution matrix.

YBLCK, ZBLCK - Dummy variables used in solving matrix

TEMP2, TEMP3, TEMP5, TEMP6, TEMP7, TEMP8 - Used for temporary storage of values needed to calculate values of ABLCK, CBLCK, and HBLCK.

DBLCK, EBLCK - Used for temporary storage values needed to calculate values of ABLCK, BBLCK and CBLCK.

V - Used for temporary storage.

CØ, PBS - Used to store CTHETC and PBSC values in reverse order for numerical integration.

Non-dimensioned Variables

Ø - N in decimal form

DLZ - ΔZ

DLZ2 - $(\Delta Z)^2$

DLZØ2 - $\Delta Z/2$

TWØDLZ - $2\Delta Z$

DLTIME - Δt (days)

N7 - Number of points to be used for each group of points in numerical integration subroutine NINT.

N6, N5 - Used in printing

Y - Initial total pesticide concentration (mass/cm^3) space.

RPT - Initial R (input) value retained.

NUMBER - Used with NUMCØL (input) to stop or continue solution for different columns or chosen situations.

AMTPIO - Amount of pesticide (mass/cm^2) moving downward past Z = -10 cm.

SURFIN - Amount of water applied at surface.

TIME - Time in days.

HØURS - Time in hours.

DAYS - Time in days.

DLCUM - Increment of water outflow (cm) at surface for this time step calculated from flux times DLTIME.

CUMFL - Sum of DLCUM values.

CUMUL - Cumulative outflow of water calculated by integration of THETA (θ) profile to and including present time.

CUMULP - Cumulative water outflow of previous time step.

CUMULD - Cumulative water outflow of present time step.

FLUXD - Flux at surface (cm/day) from CUMULD/DLTIME.

FLUXS - Flux at surface from water conductivity times hydraulic gradient.

CUMI, CUMINT - Initial total water content (cm) of column or profile.

AMØUNT - Total water content (cm) at present time.

FLUXO - Water flux across lower boundary.

FRCCUM - Fraction of total possible cumulative outflow-calculations for problem stop (after values for time step printed) if absolute value exceeds QFRACT (input).

LAST - Controls printing of values for last time step.

LSTEP - Number of time step.

ITERC, ITERS - Iteration numbers for water and pesticide calculations respectively.

ITERX - Number of times ITMAX exceeded.

LSIG, LSIGS - Numbers of points not passing EPSLØN or EPSLNC test.

LSIG1 - Number of points not passing DELTA1 test.

LSIG2 - Number of points not passing DELTA2 test.

ND - Determines value of Z 2 cm below the position where pesticide concentration ≠0.

NST - Value of Z one cm above that corresponding to value of ND.

CSURFI - Initial total pesticide concentration at surface (mass/cm^3 space).

HSURFI - Initial water pressure at surface.

TEMPI - Temporary value used in BBLCK and HBLCK calculations.

CØNDO - Water conductivity at lower boundary at present time step.

CØNDS - Water conductivity at surface at present time step.

NITER - One more iteration occurs when value of SMAX determined for each position.

NVAL - Number of values to be used in numerical integration program.

Q - Flux of pesticide at Z = -10 cm.

SUMCI - Initial amount of pesticide in solution (mass/cm^2).

SUMSI - Initial amount of adsorbed pesticide (mass/cm^2).

TØTI - Initial total amount of pesticide (mass/cm^2).

SUMCN - Amount of pesticide in solution at present time (mass/cm^2).

SUMSN - Amount of adsorbed pesticide at present time (mass/cm^2).

TØTN - Total amount of pesticide at present time (mass/cm^2).

TØTVØL - Amount of pesticide volatilized to and including present time (mass/cm^2).

FRACTV - Fraction of pesticide volatilized.

SØLVØL - Amount of solution phase transferred and/or volatilized (mass/cm^2).

ADSVØL - Amount of adsorbed phase transferred and/or volatilized (mass/cm^2).

Appendix B. Computer Program-Model Based on Diffusion and Mass Flow of Soil-Incorporated Pesticides.

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C  EVAPORATION FROM THE SOIL SURFACE WITH TIME VARIABLE WATER POTENTIAL
C  AT THE SURFACE.
C     VOLATILIZATION OF ORGANOCHLORINE INSECTICIDES FROM SOIL.
      IMPLICIT REAL*8(A-H, O-Z)
      DIMENSION HEAD(30),THETA(30),HCOND(30),CAP(30)
      DIMENSION HEADC(51),HCADPT(51),CAPP(51),CONP(51),A3LCK(51),B3LCK(5
     11),C3LCK(51),H3LCK(51),Y3LCK(51),Z3LCK(51),CONC(51),CAPC(51),THETA
     2C(51),HCADPI(51),Z(51),AVHEAD(51)
      DIMENSION C(51),S(51),CL(51),CPSPT(51),HYGRAD(51),CTHETC(51),THETP
     1T(51),HYHDPT(51),DV(51),DVPT(51),DVS(51),DVSPT(51),CPLUSS(51),CDPP
     2S5(51),DVIS(20),CPBSPT(51),DVSIN(20),THDSIN(20),TEMP2(51),TEMP3(51
     3),TEMP5(51),TEMP6(51),V(51),PASSV(51),E3LCK(51),F3LCK(51),P3S(51),
     4Q3(51),P3S(51),TEMP7(51),TEMP8(51),ETIME(500),TETMAT(500),FLXMAT(
     5500),SMAX(51),CTHCPI(51),P8SPT(51),CTHEPT(51),CGPAD(51)
      REAL*8 K
C  FUNCTIONS FOR BOUNDARY CONDITIONS AT SOIL SURFACE FOR WATER AND
C  PESTICIDE TRANSFER.
      SURFCE(A,B,C) = A * DEXP(B*C)
C  FUNCTIONS PERTAINING TO ADSORPTION OR DESORPTION OF PESTICIDE.
      PBADS(D) = 1./(1.+PB*K/D)
      PBDES(A,B,C)=1./(1.+PB*(K/B)**EXPON*(A/C)**(1.-EXPON))
      NUMBER = 0
C  READ IN INITIAL INFORMATION
      READ(5,998) N,ITMAX,LPRTC,NUMCOL,EPSLON,EPSLNC,R,DELTA1,DELTA2,JFR
     1ACT,CM,TIMEMX
C  READ INITIAL CONCENTRATION OF MATERIAL(CONMAT) IN MASS/UNIT MASS OF
C  SOIL, DEPTH OF INITIAL DISTRIBUTION IN CM, BULK DENSITY(GM/CC)OF SOIL
C  (PB), K(CC(LIQ)/GM SOIL), NO. OF POINTS IN TOTAL APPARENT DIFF. COEFF
C  TABLE(NOVSPT), DO NOT EXCEED NO. OF VALUES GIVEN IN DIMENSION STAT.
C  NO. (IN) OF SETS OF RELATED VALUES OF PRESSURE HEAD(HEAD), VOLUMETRIC
C  WATER CONTENT(THETA), WATER CONDUCTIVITY(HCOND), AND SPECIFIC WATER
C  CAPACITY(CAP).
      READ(5,997) CONMAT,DEPTH,PB,K,EXPON,NOVSPT,IN
      READ(5,995) ACONST
C  READ TOTAL APPARENT DIFF. COEFF. VALUES(DVSIN) (CM2/DAY) AND CORRES-
C  PONDING THETA VALUES(THDSIN) (CC LIQ/CC SPACE).
      READ(5,976)(DVSIN(J), THDSIN(J), J = 1,NOVSPT)
      READ(5,996)(HEAD(J),THETA(J),HCOND(J),CAP(J),HEAD(J+1),THETA(J+1),
     1HCOND(J+1),CAP(J+1),J = 1,IN,2)
C  INITIAL CALCULATIONS
      D = N
      DLZ = CM / D
      DLZZ = DLZ * DLZ
      DLTIME = R * DLZZ
      DLZ2 = DLZ * 0.5
      TWODLZ = DLZ + DLZ
      N1 = N + 1
      NM1 = N - 1
      N7 = N/5
      N6 = N / 2
      N5 = N6 + 1
      Z(1) = -CM
      Y = CONMAT * PB
```

```
      RPT = R
      DO 3 J = 1,N1
      Z(J+1) = Z(J) + DLZ
      HEADPI(J) = -300. - Z(J)
    3 HYHDPT(J) = HEADPI(J)
      CALL INTLY(HCOND,IN,HEAD,IN,CONC,N1,HEADPI,N1,1,N1)
      CALL INTLY(CAP,IN,HEAD,IN,CAPC,N1,HEADPI,N1,1,N1)
      CALL INTLY(THETA,IN,HEAD,IN,THETAC,N1,HEADPI,N1,1,N1)
C  PRINT BEGINNING INFORMATION
      WRITE (6,999)
C  PRINT INITIAL RUN INFORMATION
      WRITE(6,971) N,ITMAX,NUMCOL,EPSLON,QFRACT,CM,DLZ,R,TIMEMX,DLTIME,
     1EPSLNC,DELTA1,DELTA2,LPRTC
      WRITE(6,994)(HEAD(J),THETA(J),HCOND(J),CAP(J),J = 1,IN)
C  CORRECT DVS VALUES FROM 30C TO 23C TO COINCIDE WITH TEMP. APPLIC-
C  ABLE TO WATER COND. VALUES.
      DO 10 J = 1,NDVSPT
      DVIN(J) = DVSIN(J)
   10 DVSIN(J) = DVIN(J) *.5
      DO 11 J = 1,N1
      DV(J) = CONC(J)
      DVPT(J) = CAPC(J)
   11 THETPT(J) = THETAC(J)
    1 NUMBER = NUMBER + 1
      AMTPID = 0.
      SURFIN = 0.
      R = RPT
      TIME = 0.
      HOURS = 0.
      DAYS = 0.
      DLTIME = R * DLZ2
      CUMEL = 0.
      LAST = 0
      LSTEP = 0
C  CLEAR MEMORY BLOCKS
      DO 2 J = 1,N1
      CO(J) = 0.
      PBS(J) = 0.
      SMAX(J) = 0.
      CPBSPI(J) = 0.
      CTHEPI(J) = 0.
      CTHEPT(J) = 0.
      PBSPT(J) = 0.
      PDREV(J) = 0.
      TEMPB(J) = 0.
      CGRAD(J) = 0.
      CTHETC(J) = 0.
      C(J) = 0.
      CL(J) = 0.
      PBSC(J) =0.
      S(J) = 0.
      DVS(J) = 0.
      DVSPT(J) = 0.
```

```
      DBLCK(J) = 0.
      CPLUSS(J) = 0.
      CPSPT(J) = 0.
    2 COPPBS(J) = 0.
      DO 23 J = 1,NI
      HEADPI(J) = HYHDPT(J)
      CONC(J) = DV(J)
      CAPC(J) = DVPT(J)
      THETAC(J) = THETPT(J)
      HEADC(J) = HEADPI(J)
      HEADPT(J) = HEADPI(J)
      HYHEAD(J) = HEADPI(J) + Z(J)
      CAPP(J) = CAPC(J)
   23 CONP(J) = CONC(J)
C  CALCULATE HYDRAULIC GRADIENT VALUES(HYGRAD)FOR EACH Z VALUE.
      CALL DUZZ(Z,NI,HYHEAD,NI,HYGRAD,NI,0,0,1,5,NI-0.,0)
C  INITIAL PORE VELOCITY.
      DO 6 J = 1,N
      ABLCK(J) = (CONC(J) + CONC(J+1) + CONP(J) + CONP(J+1))* .25
    6 POREV(J) = (-ABLCK(J))*HYGRAD(J)/THETAC(J)
      FLUXS = (-ABLCK(N))*((3.*HEADC(N1)-4.*HEADC(N) + HEADC(NM1))/(TWOD
     1LZ) + 1.)
      POREV(N1) = FLUXS / THETAC(N1)
C  NUMERICAL INTEGRATION FOR INITIAL TOTAL LIQUID CONTENT(CUMI).
      CALL MINT (THETAC,N1,CUMI  ,DLZ,N7)
      CUMUL = 0.
      CUMINT = CUMI
      ND = (CM + DLZ - DEPTH) / DLZ + .2
      CALL MATCHV(DVS,N,20,THDSIN,20,DVS,N1,THETAC,N1,ND,N1)
C  CALCULATE INITIAL SOLUTION AND ADSORBED PHASE CONCENTRATIONS
      DO 5 J = ND,NI
      TEMPB(J) = DLZ02*POREV(J)*PBKADS(THETAC(J))
      DVSPT(J) = DVS(J)
      CTHETC(J) = Y*PBKADS(THETAC(J))
      CTHEPI(J) = CTHETC(J)
      CTHEPT(J) = CTHETC(J)
      PBSC(J) = Y - CTHETC(J)
      PBSPT(J) = PBSC(J)
      CL(J) = CTHETC(J) / THETAC(J)
      C(J) = CTHETC(J) / PB
      S(J) = CONMAT - C(J)
      SMAX(J) = S(J)
      CPLUSS(J) = CONMAT
      CPBSPI(J) = Y
      COPPBS(J) = Y
    5 CPSPT(J) = Y
      CSUMI = COPPBS(N1)
C  NUMERICAL INTEGRATION FOR INITIAL CONDITIONS.
      I = NI
      NVAL = NI - ND + 1
      DO 7 J = 1,NVAL
      PBS(J) = PBSC(I)
      CP(J) = CTHETC(I)
```

```
    7 I = I - 1
      N2 = NVAL / 5
      CALL NINT(CO,N1,SUMC1,DLZ,N2)
      CALL NINT(PBS,N1,SUMSI,DLZ,N2)
      TOTI = SUMCI + SUMSI
      IF(NUMBER.GT.1) GO TO 24
C  PRINT RESULTS PERTAINING TO INITIAL TIME.
      WRITE(6,990)(Z(J),HEADC(J),THETAC(J),HYHEAD(J),POREV (J),Z(J+N6),
     1HEADC(J+N6),THETAC(J+N6),HYHEAD(J+N6),POREV (J+N6), J = 1,N5)
      WRITE(6,986) CUMI,CUMINT
      WRITE(6,973)
      WRITE (6,993) (DVSIN(J),THDSIN(J),J=1,NDVSPT)
      WRITE(6,977)(Z(J),C(J),S(J),CPLUSS(J),    CL(J),CTHETC(J),PBSC (J)
     1,COPPBS(J),SMAX(J),DVS(J),J=ND,N1)
      WRITE(6,976) SUMCI,SUMSI,TOTI
C  STORE TOTAL AMOUNT OF MATERIAL VALUES(TOTMAT-MASS/SQ CM SOIL) AND CO-
C  RRESPONDING TIME VALUES(ETIME-DAYS) FOR CALCULATING FLUX RATES BY NUM
C  ERICAL DIFFERENTIATION USING SUBROUTINE DUZZ.
   24 ETIME(1) = TIME
      TOTMAT(1) = TOTI
      NPTS = 1
      HSURFI = HEADPI(N1)
C  TIME ADVANCE
   25 TIME = TIME + DLTIME
      IF(TIMEMX - TIME) 26,27,27
   26 TIME = TIME - DLTIME
      DLTIME = TIMEMX - TIME
      R = DLTIME/DLZZ
      TIME = TIMEMX
   27 LSTEP = LSTEP + 1
      DO 4 J = 2,N
      TEMP2(J) = HEADPI(J+1) - HEADPI(J)
    4 TEMP3 (J) = HEADPI(J) - HEADPI(J-1)
      HOURS = TIME * 24.
      DAYS = TIME
      ITERC = 0
      ITERXS = 0
C  NO FLUID ACROSS LOWER BOUNDARY
      YBLCK(1) = 1.
      ZBLCK(1) = DLZ
C  UPPER BOUNDARY CONDITION FOR WATER TRANSFER.
   28 HEADPI(N1) = SURFCE(HSURFI,ACONST,TIME)
C  LIMIT WATER PRESSURE AT SURFACE TO BE GREATER THAN SMALLEST VALUE IN
C  INPUT DATA TABLE.
      IF(HEADPI(N1).LT.HEAD(IN)) HEADPI(N1) = HEAD(IN)
      HEADC(N1) = HEADPI(N1)
C  ITERATION ADVANCE
   30 ITERC = ITERC + 1
      IF(ITERC - ITMAX) 35,35,31
   31 ITERXS = ITERXS + 1
      GO TO 65
C  LOOK UP MATRIX COEFFICIENTS
   35 CALL INTLY(HCOND,IN,HEAD,IN,CONC,N1,HEADPI,N1,1,N1)
```

```
      CALL INTLY(CAP,IN,HEAD,IN,CAPC,N1,HEADPI,N1,1,N1)
      ABLCK(1) = (CONC(1) + CONC(2) + CONP(1) + CONP(2))*  .25
      DO 36 J = 2,N
      ABLCK(J) = (CONC(J) + CONC(J+1) + CONP(J) + CONP(J+1))* .25
      CBLCK(J-1) = ABLCK(J)
      TEMP1 = (CAPC(J) + CAPP(J))/R
      ABLCK(J-1) = ABLCK(J-1) + CBLCK(J-1) + TEMP1
      TEMP4 = CBLCK(J-1) - ABLCK(J-1)
   36 HBLCK(J-1) = CBLCK(J-1)*TEMP2(J)-ABLCK(J-1)*TEMP3(J)+TWODLZ*TEMP4+
     1TEMP1 * HEADPI(J)
   37 HBLCK(NM1) = HBLCK(NM1) + CBLCK(NM1) * HEADPI(N1)
C  SOLVE SYSTEM
   41 CALL TRIDAG(ABLCK,N,BBLCK,N,CBLCK,N,HBLCK,N,YBLCK,N,ZBLCK,N,HEADC,
     1N1,2,N)
      HEADC(1) = (4. * HEADC(2) - HEADC(3) + TWODLZ) / 3.
      LSIG = 0
C  EPSILON TEST
      DO 38 J = 1,N
      TEST = HEADC(J) - HEADPI(J)
      IF(DABS(TEST)-EPSLON) 38,38,39
   39 LSIG = LSIG + 1
   38 CONTINUE
   42 DO 43 J = 1,N1
   43 HEADPI(J) = HEADC(J)
      IF(LSIG) 65,65,30
   65 CALL INTLY(THETA,IN,HEAD,IN,THETAC,N1,HEADPI,N1,1,N1)
      DO 60 J = 1,N1
      TEMP3(J) = TEMP8(J)
   60 HYHEAD(J) = Z(J) + HEADC(J)
      CUMULP = CUMUL
C  NUMERICAL INTEGRATION
      CALL NINT (THETAC,N1,CUMUL ,DLZ,N7)
      AMOUNT = CUMUL
      CUMUL = CUMI - AMOUNT
      FRCCUM = CUMUL / CUMINT
      CUMULD = CUMUL - CUMULP
      FLUXD = CUMULD / DLTIME
C  CALCULATE HYDRAULIC GRADIENT VALUES(HYGRAD)FOR EACH Z VALUE.
      CALL DUZZ(Z,N1,HYHEAD,N1,HYGRAD,N1,0,0,1,5,N1,0.,0)
      COND0 = ABLCK(1)
      CONDS = ABLCK(N)
      ABLCK(N1) = ABLCK(N)
C  BEGIN CALCULATIONS PERTAINING TO SOLUTION AND ADSORBED PHASES OF
C  CHEMICAL APPLIED TO SOIL.
C     NO CALCULATIONS FROM Z(1) TO Z(J-2) WHEN C AND S EQUAL 0 FROM Z(1)
C     THROUGH Z(J).
      DO 59 J = 1,N1
      IF(CPSPT(J)) 59,59,62
   59 CONTINUE
   62 ND = J - 2
      IF(ND.LT.1) ND = 1
      NST = ND + 1
C  CALCULATE AVERAGE VELOCITY IN PORES.
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```
      DO 61 J = 1,ND
   61 POREV(J) = (-ABLCK(J))*HYGRAD(J)/THETAC(J)
      DO 611 J = NST,N1
      POREV(J) = (-ABLCK(J))*HYGRAD(J)/THETAC(J)
      IF(HEADPI(J) + 1.D+5) 612,611,611
  612 POREV(J) = POREV(J)*(HEAD(IN)-HEADPI(J))/HEAD(IN)
  611 CONTINUE
C     SURFACE BOUNDARY CONDITIONS
   45 FLUXS =  (-ABLCK(N)) * HYGRAD(N1)
   47 IF(CSURFI) 64,64,69
   69 IF(TIME - .95) 63,64,64
   63 COPPBS(N1) = SURFCE(CSURFI,(-2.0D1),TIME)
      CTHEPI(N1) = COPPBS(N1)*PBKDES(SMAX(N1),THETAC(N1),CTHEPI(N1))
      PBSC(N1) = COPPBS(N1) - CTHEPI(N1)
      GO TO 66
   64 CTHETC(N1) = 0.
      CTHEPI(N1) = 0.
      PBSC(N1) = 0.
      COPPBS(N1) = 0.
C  LOWER BOUNDARY CONDITIONS.
   66 CTHETC(ND) =0.
      COPPBS(ND) = 0.
      CPPSPI(ND) = 0.
      CTHEPI(ND) = 0.
      PBSC(ND) = 0.
      TEMP1 = 2. / R
      CALL INTLC(DVSIN,20,THDSIN,20,DVS,N1,THETAC,N1,ND,N1)
      DBLCK(ND) = (DVS(ND)+DVS(NST)+DVSPT(ND)+DVSPT(NST))*.25
      DO 67 J = NST,N
      TEMP6(J) = CPSPT(J) - CPSPT(J-1)
      TEMP7(J) = CPSPT(J+1) - CPSPT(J)
      DBLCK(J) = (DVS(J)+DVS(J+1)+DVSPT(J)+DVSPT(J+1))*.25
      EBLCK(J-1) = DBLCK(J)
   67 BBLCK(J-1) = DBLCK(J-1) + EBLCK(J-1) + TEMP1
C  IF MATERIAL REACHES THE LOWER BOUNDARY OF THE SOIL COLUMN OR PROFILE,
C  NO MATERIAL CROSSES THE BOUNDARY.
      IF(NST - 2) 320,320,321
  320 YBLCK(1) = 1.
      ZBLCK(1) = 0.
      GO TO 322
  321 YBLCK(ND) = 0.
      ZBLCK(ND) = 0.
  322 NITER = 0
      ITERS = 0
C  ITERATION ADVANCE
  100 ITERS = ITERS + 1
      IF(ITERS - ITMAX) 102,102,50
  102 DO 68 J = ND,N1
      IF(PBSPT(J) - PBSC(J)) 681,68 ,682
  681 TEMP3(J) = DLZ02*POREV(J)*PBKADS(THETAC(J))
      GO TO 68
  682 IF(CTHEPI(J).LE.0..OR.SMAX(J).LE.0.) GO TO 681
      TEMP3(J) = DLZ02*POREV(J)*PBKDES(SMAX(J),THETAC(J),CTHEPI(J))
```

```
   68 ABLCK(J) = DBLCK(J) + TEMP3(J)
      DO 32 J = NST,N
      CBLCK(J-1) = FBLCK(J-1) - TEMP3(J+1)
   32 HBLCK(J-1) = TEMP1*CPSPT(J)+EBLCK(J-1)*TEMP7(J)-DBLCK(J-1)*TEMP6(J
     1)-TEMP8(J+1)*CPSPT(J+1)+TEMP5(J-1)*CPSPT(J-1)
      HBLCK(NM1) = HBLCK(NM1) + CBLCK(NM1) * CPBSPI(N1)
C  SOLVE SYSTEM
      CALL TRIDAG(ABLCK,N,BBLCK,N,CBLCK,N,HBLCK,N,YBLCK,N,ZBLCK,N,COPPBS
     1,N1,NST,N)
      COPPBS(1) = (4.*COPPBS(2)-COPPBS(3))/3.
C  EPSILON TEST
      LSIGS = 0
      DO 109 J = NST,N
      IF(COPPBS(J).LT.1.D-3) COPPBS(J) = 0.
      TEST = COPPBS(J) - CPBSPI(J)
      IF(DABS(TEST)-EPSLNC) 109,109,108
  108 LSIGS = LSIGS + 1
  109 CONTINUE
      DO 111 J = NST,N1
      CPBSPI(J) = COPPBS(J)
      IF(COPPBS(J)) 1100,1100,1102
 1100 CTHETC(J) = 0.
      PBSC(J) = 0.
      GO TO 111
 1102 PBSC(J) = COPPBS(J) - CTHEPI(J)
      IF(PBSPT(J) - PBSC(J)) 1106,1101,1107
 1101 CTHETC(J) = COPPBS(J)-CPSPT(J)+CTHEPT(J)
      GO TO 111
 1106 CTHETC(J) = COPPBS(J)*PBKADS(THETAC(J))
      PBSC(J) = COPPBS(J)  - CTHETC(J)
      SMAX(J) = PBSC(J) / PB
      GO TO 111
 1107 IF(CTHEPI(J)) 1100,1100,1108
 1108 IF(SMAX(J)) 1106,1106,1105
 1105 CTHETC(J) = COPPBS(J)*PBKDES(SMAX(J),THETAC(J),CTHEPI(J))
      PBSC(J) = COPPBS(J)  - CTHETC(J)
  111 CTHEPI(J) = CTHETC(J)
      IF(LSIGS) 100,49,100
   49 NITER = NITER + 1
      DO 1104 J = ND,N1
      IF(PBSPT(J) - PBSC(J)) 1103,1103,1104
 1103 SMAX(J) = PBSC(J) / PB
 1104 CONTINUE
      IF(NITER - 1) 50,100,50
C  DELTA TESTS AND DELTA TIME CHANGES
   50 GO TO (54,112),M
   54 LSIG1= 0
      LSIG2 = 0
      DO 51 J = NST,N
      TEST = COPPBS(J) - CPSPT(J)
      IF(DABS(TEST)-DELTA1) 51,51,52
   52 LSIG1 = LSIG1 + 1
      IF(DABS(TEST)-DELTA2) 51,51,53
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   53 LSIG2 = LSIG2 + 1
   51 CONTINUE
      IF(LSIG1) 55,112,55
C  DELTA TIME TOO LARGE
   55 IF(LSIG2) 56,112,56
   56 TIME = TIME - DLTIME
      DLTIME = DLTIME * 0.75
      IF(DLTIME-1.D-5) 561,562,562
  561 DLTIME = DLTIME / 0.75
      TIME = TIME + DLTIME
      GO TO 112
  562 LSTEP = LSTEP - 1
      DO 57 J = 1,N1
      CTHEPI(J) = CTHEPT(J)
      CPBSPI(J) = CPSPT(J)
      PBSC(J) = PBSPT(J)
   57 HEADPI(J) = HEADPT(J)
      R = R * 0.75
      GO TO 25
C  NUMERICAL INTEGRATION
  112 I = N1
      NVAL = N1 - ND + 1
      IF(NVAL-13) 113,113,114
  113 N2 = 2
      GO TO 121
  114 IF(NVAL-18) 115,115,116
  115 N2 = 3
      GO TO 121
  116 IF(NVAL-23) 117,117,118
  117 N2 = 4
      GO TO 121
  119 IF(NVAL-28) 119,119,120
  119 N2 = 5
      GO TO 121
  120 N2 = 6
  121 DO 8 J = 1,NVAL
      PBS(J) = PBSC(I)
      CO(J) = CTHETC(I)
    8 I = I - 1
      CALL NINT(CO,N1,SUMCN,DLZ,N2)
      CALL NINT(PBS,N1,SUMSN,DLZ,N2)
      Q=(-DBLCK(20))*(CDPPBS(19)-4.*CDPPBS(20)+3.*CDPPBS(21))/TWODLZ+POR
     1EV(21)*CTHETC(21)
      IF(Q) 12,13,13
   12 AMTP10 =DABS(Q) * DLTIME + AMTP10
   13 TOTN = SUMCN + SUMSN
      TOTVOL = TOTI -TOTN
      FRACTV = TOTVOL / TOTI
      DLCUM = POREV(N1)*THETAC(N1)*DLTIME
      CUMFL = CUMFL + DLCUM
C.............PRINT RESULTS.............
C  PRINT RESULTS FOR FIRST TIME.
      IF(LSTEP - 1) 72,72,70
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```
   70 IF(TIME - .2) 95,71,71
C  PRINT RESULTS FOR EACH SELECTED TIME (ACCORDING TO VALUE OF LPRTC).
   71 IF((LSTEP/LPRTC)*LPRTC.NE.LSTEP) GO TO 73
   72 WRITE (6,973)
      FLUXD = (-CONDD) *  ((4.*HEADC(2) - HEADC(3) - 3.*HEADC(1))/(TWODL
     1Z) + 1.)
      FRFCUM = CUMFL / CUMINT
      CHGFLX = SURFIN
      CALL DUZZ(Z,N1,COPPBS,N1,CGRAD,N1,0,0,1,5,N,0.,0)
      CGRAD(N1) = (COPPBS(NM1)-4.*COPPBS(N)+3.*COPPBS(N1))/ TWODLZ
      DO 76 J = ND,N1
      V(J) = (-DBLCK(J-1))*CGRAD(J)
      CO(J) = POREV(J) + CTHETC(J)
      PBS(J) = V(J) + CO(J)
      CPLUSS(J) = COPPBS(J) / PB
      C(J) = CTHETC(J) / PB
      S(J) = CPLUSS(J) - C(J)
   76 CL(J) = CTHETC(J) / THETAC(J)
      SOLVOL = SUMCI - SUMCN
      ADSVOL = SUMSI - SUMSN
      N3 = (N1 - ND) / 2
      N4 = ND + NVAL / 2
      WRITE(6,992) ITERC,LSIG,LSTEP,TIME,DLTIME
      WRITE(6,989) HOURS,DAYS,FLUXD,CUMFL,CUMUL,ITERXS,FLUXD
      WRITE(6,985) FRCCUM,FRFCUM,CONDS,FLUXS
      WRITE(6,981) AMOUNT,SURFIN,CHGFLX
      WRITE(6,990)(Z(J),HEADC(J),THETAC(J),HYHEAD(J),POREV (J),Z(J+N6),
     1HEADC(J+N6),THETAC(J+N6),HYHEAD(J+N6),POREV (J+N6), J = 2,N5,2)
      WRITE(6,977)(Z(J),C(J),S(J),CPLUSS(J),     CL(J),CTHETC(J),PBSC (J)
     1,COPPBS(J),SMAX(J),DVS(J),J=ND,N1)
      WRITE(6,984) ( Z(J),V(J),CO(J),PBS(J),CGRAD(J),Z(J+N3),V(J+N3),CO(
     1J+N3),PBS(J+N3),CGRAD(J+N3),J=ND,N4)
      WRITE(6,975) SOLVOL,ADSVOL,TOTVOL
      WRITE(6,968) ITERS,LSIGS
      WRITE(6,967) FRACTV
      WRITE(6,991) AMTP10
      WRITE(6,976) SUMCN,SUMSN,TOTN
      WRITE (6,964) N2
C  END TEST
      IF(LSTEP-1) 73,73,74
   74 NPTS = NPTS + 1
      ETIME (NPTS) = TIME
      TOTMAT(NPTS) = TOTN
   73 IF(FRACTV - QFRACT) 90,91,91
   90 IF(TIMEMX - TIME) 91,91,92
   92 IF(DABS(FRCCUM)-QFRACT) 95,91,91
   91 IF(LAST) 98,94,98
   94 LAST = 1
      IF((LSTEP/LPRTC)*LPRTC.EQ.LSTEP) GO TO 98
C  PRINT RESULTS FOR LAST TIME.
      GO TO 72
C  SET UP BLOCKS FOR NEXT TIME
   95 CALL INFLY(HCOND,IN,HEAD,IN,CONC,N1,HEADPI,N1,1,N1)
```

```
      CALL INTLY(CAP,IN,HEAD,IN,CAPC,N1,HEADPI,N1,1,N1)
      DO 96 J = 1,N1
      CO(J) = 0.
      PBS(J) = 0.
      TEMPB(J) = TEMP3(J)
      DVSPI(J) = DVS(J)
      PBSPI(J) = PBSC(J)
      CTHEPI(J) = CTHETC(J)
      CTHEPT(J) = CTHETC(J)
      CPSPI(J) = COPPBS(J)
      CPBSPI(J) = COPPBS(J)
      CAPP(J) = CAPC(J)
      CONP(J) = CONC(J)
   96 HEADPT(J) = HEADC(J)
C  DELTA TIME TOO SMALL
      IF(LSIG1.EQ.0.AND.LSIGS.EQ.0) GO TO 254
      GO TO 25
  254 R = R + R
      DLTIME = DLTIME + DLTIME
      GO TO 25
   98 LSIG1 = 1
C  CALCULATE FLUX RATES(FLXMAT-MASS/SQ CM/DAY)
   81 CALL DUZ2(ETIME,NPTS,TOTMAT,NPTS,FLXMAT,NPTS,0,0,1,5,NPTS,0.,0)
      WRITE (6,973)
      WRITE(6,965)(ETIME(J),TOTMAT(J),FLXMAT(J), J = 1,NPTS)
      WRITE(6,974) CONMAT,PB,K,DEPTH
  101 IF(NUMBER - NUMCOL) 1,99,99
   99 CALL EXIT
  964 FORMAT ('+',126X,I5)
  965 FORMAT ('0',2X,3('  TIME(DAYS)    MASS/SQ CM  MASS/SQ CM/DAY')/('
     1',1P9E14.3))
  967 FORMAT(' ','FRACTION VOLATILIZED',25X,1PE13.3)
  968 FORMAT('+',65X,'ITER. NO.',I3,'  NO. OF POINTS NOT PASSING TEST',I
     14)
  971 FORMAT('0','NO. OF INTERVALS',I4,'  MAX. NO. OF ITERATIONS',I3,'
     1NO. OF COLUMNS',I3,'  EPSILON =',1PE10.2,'  FRACTION OF OUTFLOW FO
     2R STOP',E10.2/' ','LENGTH OF COLUMN',1PE10.2,' CM  DELTAZ',E10.2,'
     3 CM  INITIAL R',E10.2,'  MAX. TIME',E10.2,' DAYS  INITIAL DELTA TI
     4ME',E10.2/' ','EPSILON TEST VALUE FOR  ITERATION  DIFFERENCES =',1
     5PE9.2,'  MIN. DIFFERENCE =',E9.2,'  MAX. DIFFERENCE =',E9.2,' PRIN
     6T INTERVALS ',I2)
  973 FORMAT('1')
  974 FORMAT('0','INITIAL MASS/GM SOIL',1PE11.3,'  BULK DENSITY',E9.2,'
     1GM/CC','  K',E11.3,' CC(LIQ)/GM SOIL'/' ','DEPTH OF INITIAL DISTRI
     2BUTION',0PF5.0,' CM')
  975 FORMAT('0','MASS/CM2 SOIL TRANSFERRED FROM SOLUTION PHASE',1PE13.3
     1/' ','MASS/CM2 SOIL TRANSFERRED FROM ADSORBED PHASE',1PE13.3/' ','
     2TOTAL MASS/CM2 SOIL VOLATILIZED',14X,1PE13.3)
  976 FORMAT(' ',12X,'MASS/CM2 SOIL IN SOLUTION',1PE13.3,' MASS/CM2 SOIL
     1 ADSORBED',E13.3,' TOTAL MASS/CM2 SOIL',E13.3)
  977 FORMAT('0',7X,'Z',12X,'C',12X,'S',10X,'C + S',8X,' CL ',11X,'C',12
     1X,'S',10X,'C + S',10X,'SM',11X,'DVS'/' ',7X,'CM',18X,'MASS/GM SOIL
     2',14X,'MASS/CC(LIQ)',13X,'MASS/CC(TOTAL)',17X,'MASS/GM',6X,'CM2/DA
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```
   3Y'/(' ',1P10E13.3))
978 FORMAT (8E10.3)
980 FORMAT(2F10.0,3E10.3,F10.0)
981 FORMAT   (' AMOUNT IN PROFILE AT THIS TIME',1PE11.3,' CM ','FLUID
   1APPLIED AT Z=0 TO THIS TIME',E11.3,' CM  ','NET GAIN OR LOSS BY FL
   2UX',E11.3,' CM')
982 FORMAT (4E10.3)
983 FORMAT (2F10.3)
984 FORMAT(' ',48X,'TRANSFER OF MATERIAL-MASS/SQ CM/DAY'/' ',2(8X,'Z',
   17X,'DIFFUSION',4X,'BY WATER',7X,'TOTAL',6X,'CONC. GRAD')/(2(1PE13.
   22,4E13.3)))
985 FORMAT(' ','Q/QINF. BY INTEGRAL',1PE11.3,'  Q/QINF. BY DIFFERENCE'
   1,E11.3,'   AVE. K AT SURFACE',E11.3,'  FLUX AT SURFACE',E11.3)
986 FORMAT('0','INITIAL CUMULATIVE WATER',1PE11.3,'  INFINITE OUTFLOW'
   1,E11.3)
989 FORMAT('0','TIME IS',1PE11.3,' HOURS  OR',F11.3,' DAYS  FLUX OUT',
   1E11.3,' CM/DAY.  CUMULATIVE OUTFLOW FROM FLUX',E11.3,' CM'/' CUMUL
   2ATIVE OUTFLOW FROM THETA PROFILE',1PE11.3,' CM  NO. OF TIMES OVERI
   3TERATED',I4,' FLUX BY CUMULATIVE DIFF.',E11.3)
990 FORMAT('0',2(8X,'Z',5X,'PRESSURE HEAD',' WATER CONTENT',' HYD. HE
   1AD  ',' PORE VEL.')/(2(1PE13.2,4E13.3)))
991 FORMAT ('+',65X,'AMOUNT DOWNWARD PAST Z= -10 CM.',1PE16.3)
992 FORMAT('0','ITER. NO.',I3,'  NO. OF POINTS NOT PASSING TEST',I5,I5
   1,' TIME STEP  TIME',1PE11.3,' DAY.  DELTA TIME',E11.3,' DAY.')
993 FORMAT('0',13X,'EXPERIMENTAL VALUES OF APPARENT DIFFUSION  COEFFIC
   1IENTS(DVS) WITH CORRESPONDING WATER CONTENT VALUES(THETA).'/' ',52
   2X,'DVS(CM2/DAY',4X,'THETA(CM/CM)'/(' ',46X,1P2E16.3))
994 FORMAT(' ',2(10X,'HEAD',12X,'THETA',7X,'CONDUCTIVITY',6X,'CAPACITY
   1')/' ',2(11X,'CM',13X,'CM/CM',10X,'CM/DAY',11X,'1/CM  ')/(' ',1PE1
   27.3,7E16.3))
995 FORMAT(E10.5)
996 FORMAT(8E10.3)
997 FORMAT(2F10.0,F10.2,2F10.3,2I5)
998 FORMAT(I4,3I2,6E10.3,2F5.0)
999 FORMAT('1','EVAPORATION OF WATER FROM THE SOIL SURFACE WITH NO FLO
   1W OF FLUID ACROSS THE LOWER BOUNDARY.  EVAPORATION RATE IS VARIABL
   2E WITH TIME.'/' ','VOLATILIZATION OF ORGANIC MATERIAL FROM THE SOI
   3L SURFACE OCCURS AFTER TIME = 0 WITH CONCENTRATION(MASS/GM SOIL) =
   4 0 AT THE SURFACE.')
    END
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C       SUBROUTINE  DUZ2 --- WILD POINT, SMOOTH, AND/OR DIFFERENTIATE.
C       SUBROUTINE TO PREFORM WILD POINT REPLACEMENT, SMOOTHING AND/OR
C     DIFFERENTIATION IN A RANDOMLY SPACED VARIABLE.  X(I) IS THE INDEPEN-
C     DENT VARIABLE, Y(I) THE DEPENDENT VARIABLE TO BE MODIFIED AND YO(I)
C     THE RESULT OF THE MODIFICATION.  Y AND YO MAY BE THE SAME OR DIFFER-
C     ENT TABLES EXCEPT THAT IF MORE THAN ONE OPTION IS SPECIFIED OR IF
C     ONE OPTION IS SPECIFIED FOR MULTIPLE USEAGE Y AND YO MUST BE THE
C     SAME TABLE.  THE OPTIONS ARE IWP=WILD POINT PASSES, ISM=SMOOTHING
C     PASSES AND IDF=DIFFERENTIATE PASSES WITH THE OPTIONS EXECUTED IN THE
C     ORDER GIVEN.  IPAR=NUMBER OF POINTS TO BE USED IN FORMING PARABOLA,
C     N=NUMBER OF X VALUES IN TABLE, WP=NUMBER OF STANDARD DEVIATIONS FOR
C     WILD POINT CRITERIA.  NANC=0 FOR NO ANCHORING, 1 TO ANCHOR FIRST
C     POINT ONLY, 2 TO ANCHOR LAST POINT ONLY, OR 3 TO ANCHOR BOTH FIRST
C     AND LAST POINTS.  NANC IS APPLICABLE ONLY FOR WILD POINTING AND/OR
C     SMOOTHING OPERATIONS.  IPAR HAS AN UPPER LIMIT OF 25, MUST   BE
C     ODD AND MUST NOT BE GREATER THAN N, NOR LESS THAN 5.
C   SUBROUTINE SUPPLIED BY UCR COMPUTER CENTER- JOHN JAMES, PRINCIPAL
C   PROGRAMMER.
        SUBROUTINE DUZ2 (X,N1,Y,N2,YO,N3,IWP,ISM,IDF,IPARI,NI,WP,NANC)
        IMPLICIT REAL*8(A-H, O-Z)
        REAL*8 X,Y,YO,XS,YS,A,B,C,D
        DIMENSION XS(25),YS(25),A(25,3),B(25),C(3,3),D(3)
        DIMENSION X(N1),Y(N2),YO(N3)
        N = NI
        IF (N - 5) 130,130,200
  200 IPAR = IPARI
        PNT1 = Y(1)
        PNTN = Y(N)
        IPAR1 = (IPAR - 1)/2
        FIPAR = IPAR - 4
        IF (IWP) 1,2,1
C IWP NON-ZERO WHEN WILD POINTING REQUIRED
    1 IMT = IWP
        M = 1
        GO TO 6
    2 IF (ISM) 3,4,3
C ISM NON ZERO WHEN SMOOTHING REQUIRED (WILD POINTING COMPLETED)
    3 IMT = ISM
        M = 2
        GO TO 6
    4 IF (IDF) 5,130,5
C IDF NON-ZERO WHEN DIFFERENTIATION REQUIRED (SMOOTHING COMPLETED)
    5 IMT = IDF
        M = 3
    6 DO 129 INP = 1,IMT
        DO 128 I = 1,N
        IF (I-1) 101,101,103
  101 DO 102 J = 1,IPAR
        XS(J) = X(J)
  102 YS(J) = Y(J)
  103 IF (I-IPAR1-1) 104,104,105
  104 IP = I
        GO TO 109
```

```
  105 IF (I + IPAR1 - N) 106,106,108
  106 DO 107 J = 2,IPAR
      XS(J-1) = XS(J)
  107 YS(J-1) = YS(J)
      J = I + IPAR1
      XS(IPAR) = X(J)
      YS(IPAR) = Y(J)
      IP = IPAR1 + 1
      GO TO 109
  108 IP = I + IPAR - N
  109 DO 110 J = 1,IPAR
      A(J,3) = 1.0
      A(J,2) = XS(J) - XS(IP)
      A(J,1) = A(J,2)*A(J,2)
  110 B(J) = YS(J)
      DO 111 J = 1,3
      D(J) = 0.0
      DO 1101 K = 1,3
 1101 C(J,K) = 0.0
  111 CONTINUE
      GO TO (112,114,114),M
  112 DO 113 J = 1,3
  113 A(IP,J) = 0.0
      B(IP) = 0.0
  114 DO 121 J = 1,3
      DO 118 K = J,3
      DO 115 L = 1,IPAR
  115 C(J,K) = C(J,K) + A(L,J) * A(L,K)
      IF (K-J) 118,118,116
  116 C(J,K) = C(J,K) / C(J,J)
      DO 117 L = 1, IPAR
  117 A(L,K) = A(L,K) -C(J,K) * A(L,J)
  118 CONTINUE
      DO 119 L = 1, IPAR
  119 D(J) = D(J) + A(L,J) * B(L)
      D(J) = D(J)/C(J,J)
      DO 120 L = 1, IPAR
  120 B(L) = B(L) - D(J) * A(L,J)
  121 CONTINUE
      GO TO (122,126,127),M
  122 SIGMA = 0.0
      DO 123 J = 1, IPAR
  123 SIGMA = SIGMA + B(J)*B(J)
      SIGMA =DSQRT (SIGMA/FIPAR)
      IF(WP*SIGMA-DABS (YS(IP)-D(3))) 126,126,125
  125 YO(I) = Y(I)
      GO TO 128
  126 YO(I) = D(3)
      GO TO 128
  127 YO(I) = D(2) - D(3) * C(2,3)
  128 CONTINUE
      GO TO(1281,1281,129),M
 1281 IF (NANC) 1282,129,1282
```

```
 1282 IF (NANC-2) 1283,1285,1284
 1283 YP(I) = PNT1
      GO TO 129
 1284 YP(I) = PNT1
 1285 YP(N) = PNTN
  129 CONTINUE
      GO TO (2,4,130),M
  130 RETURN
      END

C  LINEAR INTERPOLATION
      SUBROUTINE INTLY(Y,N,X,N1,YP,N2,XP,N3,L,L1)
      IMPLICIT REAL*8(A-H, O-Z)
      REAL*8 Y,X,YP,XP
      DIMENSION Y(N),X(N1),YP(N2),XP(N3)
      DO 5 J = L,L1
      I = 2
      IF(XP(J) - X(I)) 1,10,10
   10 YP(J) = Y(I)
      GO TO 5
    1 IF(DABS(XP(J))-DABS(X(I))) 4,3,2
    2 I = I + 1
      GO TO 1
    3 YP(J) = Y(I)
      GO TO 5
    4 YP(J) = Y(I-1)+(Y(I)-Y(I-1))/(DABS(X(I))-DABS(X(I-1)))*(DABS(XP(J
     1))-DABS(X(I-1)))
    5 CONTINUE
      RETURN
      END

C  LINEAR INTERPOLATION
      SUBROUTINE INTLC(Y,N,X,N1,YP,N2,XP,N3,L,L1)
      IMPLICIT REAL*8(A-H, O-Z)
      REAL*8 Y,X,YP,XP
      DIMENSION Y(N),X(N1),YP(N2),XP(N3)
      DO 5 J = L,L1
      I = 2
    1 IF(XP(J) - X(I)) 4,3,2
    2 I = I + 1
      GO TO 1
    3 YP(J) = Y(I)
      GO TO 5
    4 YP(J) = Y(I-1) + (Y(I) - Y(I-1)) / (X(I)-X(I-1))*(XP(J)-X(I-1))
    5 CONTINUE
      RETURN
      END
```

```
C  SOLVES TRIDIAGONAL MATRIX
      SUBROUTINE TRIDAG(A,N1,B,N2,C,N3,H,N4,Y,N5,Z,N6,V,N7,IVAL,ILAST)
      IMPLICIT REAL*8(A-H, O-Z)
      REAL*8 A,B,C,H,Y,Z,V
      DIMENSION A(N1),B(N2),C(N3),H(N4),Y(N5),Z(N6),V(N7)
      DO 1 J = IVAL,ILAST
      DENOM = B(J-1) - A(J-1) * Y(J-1)
      IF(DENOM) 11,10,11
   10 DENOM = 1.D-17
   11 Y(J) = C(J-1) / DENOM
    1 Z(J) = (H(J-1) + A(J-1) * Z(J-1))/ DENOM
      Y(ILAST) = 0.
      J = ILAST
      DO 2 I = IVAL,ILAST
      V(J) = Z(J) + Y(J) * V(J+1)
    2 J = J-1
      RETURN
      END

C  NUMERICAL INTEGRATION
      SUBROUTINE NINT(X,N,SUM,H,N7)
      IMPLICIT REAL*8(A-H, O-Z)
      REAL*8 X
      DIMENSION X(N)
      L = N7
      SUM = 0.
      DO 1 K = 1,L
      J = 5 * (K - 1)
      A = H * 5.*(19. * (X(J+1) + X(J+6)) + 75. * (X(J+2) + X(J+5)) + 50
     1. * (X(J+3) + X(J+4)))/ 288.
      SUM = SUM + A
    1 CONTINUE
      RETURN
      END
```